

**DOKLADY PHYSICAL CHEMISTRY**  
**VOLUME 116 NUMBERS 1 - 6**  
**SEPTEMBER - OCTOBER 1957**

1011311

# PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Section: PHYSICAL CHEMISTRY

Volume 116, Issues 1-6

September-October, 1957.

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(A Publication of the Academy of Sciences of the USSR)

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IN ENGLISH TRANSLATION

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CONSULTANTS BUREAU, INC.

227 West 17th Street

New York 11, N. Y.

Printed in the United States

Annual Subscription	\$160.00
Single Issue	35.00

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# SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhtI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIEŠKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.



## ON THE INTERACTION BETWEEN CARBON BLACK AND SULFUR DURING THE VULCANIZATION OF RUBBER

G. A. Blokh and A. G. Yaroshevich

(Presented by Academician P. A. Rebinder, April 3, 1957)

The mechanism of the strengthening of rubber by carbon black has until recently been interpreted from the physical point of view. According to the researches of P. A. Rebinder and co-workers [1] the extent of the interaction between the filler and the rubber is given by the decrease in the free energy of the system resulting from the wetting of  $1 \text{ cm}^2$  of the surface of the filler particles by rubber. The rubber is bound to the surface of the carbon black particles through adsorption and forms around these particles an extended film which is characterized by high strength [2]; in this state the rubber is referred to as "bound" or film-like rubber. In systems in which such adsorbed rubber is present there appears on the surface of the filler particles an effect which resembles a kind of "crystallization" of rubber which results in a strengthening of the interaction between individual chains and hence in increased strength of the rubber [3]. According to Kusov [4], at optimum filling of the rubber with carbon black the mixture constitutes a continuous mass — a molecular space lattice with carbon particles situated in its nodes.

More recent investigations of the structure and constitution of carbon blacks [5-7] make it possible to interpret the mechanism of strengthening of rubber by carbon blacks also from the chemical point of view. It has been established [6] that certain oxygen-containing active groups, namely,  $-\text{COH}$ ,  $\text{OH}$ ,  $\text{COOH}$ ,  $\text{C}=\text{O}$  are present in the structure of carbon blacks. The existence of  $\text{C}=\text{C}$  bonds has also been observed, the latter being especially characteristic of structures of oven blacks formed in atmospheres deficient in oxygen. The possibility of the participation of carbon black in the chemical reactions taking place during vulcanization also indicates their unsaturated character as shown by the fact that they are capable of adding on bromine. It has been observed [8] that the reactivity of carbon blacks as determined by the content of oxygen-containing groups (e. g., quinones) on the surface of their particles, changes markedly when the blacks are submitted to thermal treatment. Complete removal of such groups by heating the carbon black at  $800^\circ$  renders it chemically inert, and mixtures of rubber with such carbon black do not undergo any changes on heating. It has been found [9] that  $\beta$ -quinone-dioxine, p-nitrosodiphenylamine, hexachlorocyclopentadiene and other compounds act as promoters of the interaction of rubber with carbon black by giving rise to the formation of rubber molecule radicals which react with the active centers on the surface of carbon black particles with the formation of valence bonds. It appears quite probable that in the course of the vulcanization process carbon blacks interact chemically with substances which act as accelerators. In our investigations published recently [10, 11] we have given some experimental data which indicate that direct interaction of carbon black with sulfur is, indeed, taking place during the vulcanization of rubber. The application of radioactive isotopes opens up great possibilities for the investigation of this problem which is so important in the technology of rubber.

In the present paper we are giving some kinetic data on the interaction of carbon blacks (gas black, lamp-black) with sulfur and accelerators. The investigation of this problem was carried out by the following methods: (a) investigation of the interaction of radioactive sulfur with carbon black at temperatures used in vulcanization processes, (b) investigation of the adsorption of rubber molecules on the surface of carbon black particles from benzene solutions, the carbon blacks having been submitted to different thermal treatments in mixtures with sulfur and accelerators, and (c) investigation of the influence of the preliminary heat treatment of the mixture of carbon black, sulfur and accelerator on the physicochemical properties of rubbers based on different synthetic rubber polymers.

## EXPERIMENTAL

**Kinetics of the combination of radioactive sulfur with carbon black and lampblack.** We have investigated a mixture of black and sulfur  $S^{35}$  containing the two components in the proportion of 100:3, respectively. Three series of experiments were carried out.

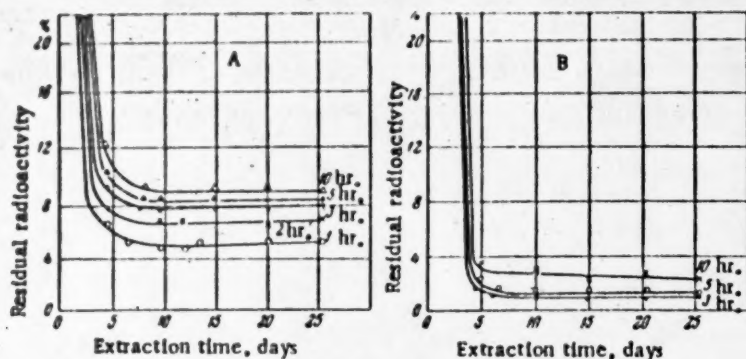


Fig. 1. Kinetics of the extraction of radiosulfur as a function of the length of heat treatment of black-sulfur mixtures at 150°: A) carbon black, B) lampblack.

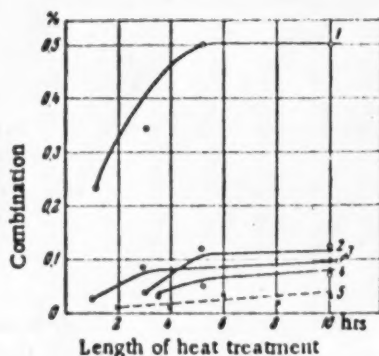


Fig. 2. Kinetics of the combination of sulfur with carbon blacks: 1) gas black (carbon black) and sulfur heated together at 150°; 2) sulfur heated at 150° and mixed with gas black; 3) lampblack and sulfur heated together at 150°; 4) sulfur heated at 150° and mixed with lampblack; 5) lampblack and sulfur, without heat treatment.

of the quantitative aspect of the adsorptional combination of sulfur with the carbon blacks. The comparison of radioactivity residual in the samples of Series I with that in samples of Series II and III enabled us to establish the true character of the chemical combination of sulfur with the blacks. Kinetic data relating to the combination of sulfur with carbon black and lampblack are presented below. From an analysis of the curves in Figs. 1 and 2 it becomes quite obvious that chemical interaction takes place between the blacks and the sulfur when the two are heated together. Even after extraction of the sulfur with benzene for 600 hours it was impossible to remove all sulfur from its mixture with the blacks. Carbon black combines chemically with sulfur to a considerably greater extent than does lampblack. Our data, obtained by making use of radioactive sulfur, are in close agreement with those obtained by Studebaker [12] who reported that on heating one part of sulfur with 9 parts of carbon black for 18 hours at 150°, 0.64% of sulfur combined chemically with the black.

**Series I.** Accurately weighed samples of the black (carbon black, lampblack) were intimately mixed with weighed samples of radiosulfur and subsequently heated at a temperature of 145° for periods of 1, 3, 5, 8, and 10 hours.

**Series II.** Accurately weighed samples of radiosulfur were heated alone at 145° for periods of 1 to 10 hours after which they were mixed with the blacks.

**Series III.** Accurately weighed samples of the blacks and radioactive sulfur were intimately mixed, but were not submitted to the heat treatment.

From each series of mixtures samples were taken for the determination of initial radioactivity. Subsequently each of these mixtures, having undergone the different individual heat treatment, was submitted to continuous extraction with benzene in the cold for 600 hours in order to remove free radiosulfur. At strictly determined intervals during the extraction samples of the blacks were withdrawn for the determination of residual radioactivity. The experiments in Series II and III permitted an explanation

**Adsorption of rubber molecules by carbon black-sulfur complexes.** It was of interest to establish to what extent the preliminary heat treatment of carbon black alone and in admixtures with vulcanization accelerators would affect the adsorption of rubber molecules from benzene solutions onto the surface of the carbon black particles. Adsorption of rubber molecules by the black results in a change in the viscosity of the rubber solution, and this may be used as a measure of the change in adsorption activity of the black with respect to the rubber as a result of the interaction of the black with the accelerator group and the formation on the surface of the black particles of new carbon black-sulfur complexes. In our experiments we have modified somewhat the procedure developed by Yurzhenko [13]. Into flasks containing 60 ml of 0.1% solution of divinylstyrene rubber there were placed: (a) 2 g of carbon black heated at 145°, (b) 2 g of carbon black mixed with 0.1 g of sulfur and heated at

145°, (c) 2 g of carbon black mixed with 0.1 g of sulfur and 0.03 g of mercaptobenzothiazole, heated at 145° for periods from 1 to 3 hours. Prior to the addition of these substances to the solutions the relative viscosity of the initial 0.1% solution of rubber SKS-30 was determined. Depending on the length of time during which the carbon blacks and their mixtures with sulfur remain in contact with the rubber solution, adsorption of rubber molecules takes place on the surface of carbon black particles resulting in a change in the viscosity of the solution. The carbon black was separated from the rubber solutions by centrifuging. The kinetic data are shown in Fig. 3.

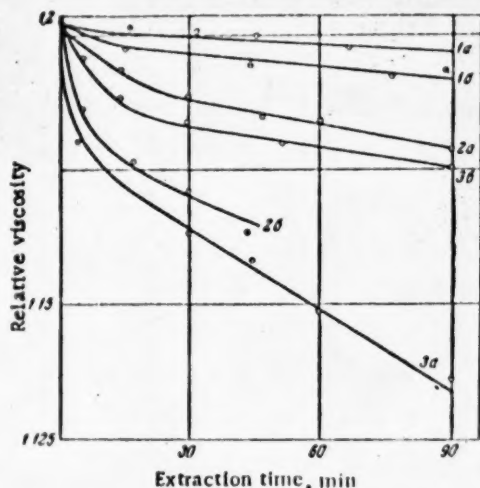


Fig. 3. Variation of the viscosity of a benzene solution of rubber SKS-30 as a function of the composition and heat treatment of the adsorbent: 1) carbon, sulfur and accelerator; 2) carbon and sulfur; 3) carbon; a) heated at 150° for 3 hours, b) without heat treatment.

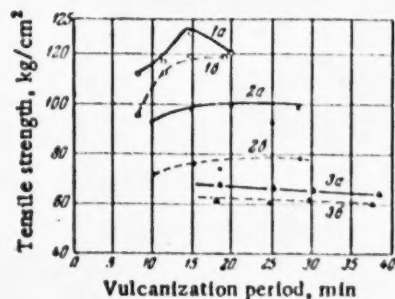


Fig. 4. The influence of preliminary heat treatment of mixtures of carbon black, sulfur and accelerators on the tensile strength of rubbers based on SKB rubber: 1) carbon black, sulfur, mercaptobenzothiazole and diphenylguanidine, 2) carbon black, sulfur and mercaptobenzothiazole, 3) carbon black, sulfur and tetramethylthiuram; a) heat treated at 130° for 120 minutes, b) not heat treated.

From the curves in Fig. 3 it will be seen that heat treatment of carbon black at 145° for periods of 1 to 3 hours increases the adsorption of rubber molecules on the surface of carbon black particles which results in a change in viscosity of the rubber solution. A different situation exists in the case of the adsorption of rubber by carbon-sulfur complexes. When the mixture of carbon, sulfur and accelerator has been heated for 3 hours the subsequent adsorption of rubber molecules on carbon black particles decreases, which manifests itself in only a negligible change in relative viscosity of the rubber solution. This result is apparently due to the formation of new carbon-sulfur complexes or of polysulfides on the surface of the blacks as a result of the interaction of the latter with the accelerator group, the effect being a decrease in the amount of rubber adsorbed on the surface of carbon black particles.

**The effect of preliminary heat treatment of carbon black, vulcanizing substances and accelerators on the strength of rubbers.** Different mixtures based on natural and synthetic rubbers were investigated. Mixtures of carbon black with sulfur and accelerators were submitted to heat treatment at 100 and 150° for different lengths of time, and were then added to the rubber mix in a mill. It was found [10, 11] that preliminary heat treatment of mixtures of carbon black with sulfur and accelerators increases the strength of the rubbers. This is of fundamental importance in the modification of the processing of rubber compounds (see Fig. 4).

We are of the opinion that vulcanizing substances and accelerators react with each other on the enormous cumulative surface of carbon black particles with the formation of intermediate polysulfidic compounds. The resultant active modifications of sulfur are not only

adsorbed physically, but enter into chemical combination with the active oxygen- and hydrogen-containing centers, with the microcrystalline structure of the carbon atom lattice and with the molecular structure of the film-like extended and oriented rubber phase on the surface of carbon black particles. The nodal points of such structures are formed not only by the rubber and sulfur, but include also carbon black which combines chemically with either constituent.

#### LITERATURE CITED

- [1] P. A. Rebinder and B. V. Margaritov, *Natural and Synthetic Rubber* 4 (1938); P. A. Rebinder, G. A. Ab and S. Ya. Weiler, *Proc. Acad. Sci. USSR* 33, 444 (1941); A. S. Kolbanovskaya, P. A. Rebinder and O. I. Lukyanova, *Colloid J.* 12, 3, 208 (1950).
- [2] A. A. Trapeznikov, *Proc. Acad. Sci. USSR* 22, 2 (1939).
- [3] P. P. Kobeko, *Amorphous Substances*, Acad. Sci. USSR Press, 1952.\*
- [4] A. B. Kusov, *Natural and Synthetic Rubber* 9 (1940).
- [5] V. V. Keltsev and P. A. Tesner, *Carbon Black*, Moscow, 1952.\*
- [6] A. M. Gessler, *Rub. Age* 1, 2 (1953); 4, 561 (1954).
- [7] J. Lander, *Rev. Gen. Caoutchouc* 30, 9, 647 (1953).
- [8] B. C. Barton, *Rub. Chem. Techn.* 28, 1 (1955).
- [9] K. Doak, *Canad. J. Techn.* 33, 1 (1955).
- [10] G. A. Blokh, *Session of the Acad. Sci. Ukr. SSR on Peaceful Uses of Atomic Energy*, Acad. Sci. Ukr. SSR Press, 1956.\*
- [11] G. A. Blokh, *Chemical Industry* 2, 14 (1956).
- [12] M. L. Studebaker, *Rub. Age* 77, 1 (1955).
- [13] A. I. Yurzhenko and I. I. Maleev, *Proc. Acad. Sci. USSR* 103, 6 (1955).

Received July 12, 1956

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# CRITICAL CONDITIONS IN THE SEDIMENTATION OF AEROSOLS IN VISCOUS FLOW AROUND A CYLINDER AND A SPHERE

G. L. Natanson

(Presented by Academician A. N. Frumkin, April 3, 1957)

Equations of motion of an aerosol particle in a stream governed by Stokes' law for the resistance of the medium have the form

$$m \frac{du_i}{dt} = 6\pi\eta R (v_i - u_i), \quad (1)$$

where  $m$  and  $R$  are the mass and radius, respectively, of the particle;  $\eta$  is the viscosity of the medium;  $t$  is the time;  $v_i$  and  $u_i$  are velocity components of the stream and of the particle in the direction of the  $i$ -axis. By virtue of their inertia the aerosol particles are displaced off the flow lines at points where the stream executes a bend. As the stream flows past an obstacle the aerosol particles suffer a displacement from the flow lines and may reach the surface of the obstacle and be adsorbed. If the velocity and position of an aerosol particle at starting time some distance away from the obstacle are known, it is possible, using Eq. (1) and assuming that  $v_i$  is a known function of the coordinates, to calculate, in principle, the path of motion of the given particle and thus to determine whether it will be adsorbed by the obstacle.

Introducing the dimensionless velocities and time,  $V_i = \frac{v_i}{v_0}$ ,  $U_i = \frac{u_i}{v_0}$  and  $\tau = \frac{v_0 t}{a}$ , where  $v_0$  is the velocity of the oncoming undisturbed stream and  $a$  is the linear dimension of the obstacle, the system of Eqs. (1) can be written in the form

$$P \frac{dU_i}{d\tau} = V_i - U_i, \quad (2)$$

where  $P = \frac{2R^2 \gamma_1 v_0}{9\eta a}$  and  $\gamma_1$  is the density of the particle. Let us assume that at some distance away from the obstacle the particle is moving in the direction of the flow lines with a velocity equal to that of the stream itself. At a given initial position of the particle its trajectory will be fully determined by the velocity field of the stream and the value of the dimensionless parameter  $P$ , often called Stokes' number. The coefficient of adsorption is given by  $\epsilon = \frac{s_1}{s_2}$ , where  $s_1$  is the cross section of a tube in the oncoming undisturbed stream bounded by the paths of particles which will just be adsorbed by the obstacle, and  $s_2$  is the median section of the obstacle; this coefficient is also fully determined by the value of  $P$  and by the velocity field of the stream. As  $P$  decreases, the limiting trajectories of just adsorbable particles approach more and more the central flow line of the stream and the value of  $\epsilon$  decreases. For each velocity field there exists a critical value of  $P = P_{cr}$  below which the coefficient of adsorption  $\epsilon$  is equal to zero ( $\epsilon = 0$ ).

Critical values of  $P$  for potential flow around obstacles in the case of plane-symmetrical and axial flow have been determined analytically by L. M. Levin [1] who showed that under these conditions the following relationship holds:

$$\frac{1}{P_{cr}} = -4 \left( \frac{\partial v_x}{\partial X} \right)_{X=-1, Y=0, Z=0} \quad (3)$$

where  $X = \frac{x}{a}$ ,  $Y = \frac{y}{a}$  and  $Z = \frac{z}{a}$  are dimensionless coordinates; in this case the origin of the axes of coordinates is taken at the center of the obstacle and the stream flows in the direction of increasing values of  $x$ . Davies and Peetz [2] have - without well-founded reasons - used Expression (3) to calculate  $P_{cr}$  in the case of viscous flow around a cylinder. However, from boundary conditions of viscous flow around bodies (at all points on the surface of the obstacle  $v_1 = 0$ ) it follows that, assuming the central (axial) flow line of the stream to be perpendicular to the surface of the obstacle, at the critical point ( $X = -1$ ,  $Y = 0$ ,  $Z = 0$ ) we have  $\partial v_y / \partial y = \partial v_z / \partial z = 0$ , whence, taking into account the equation of incompressibility  $\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0$ , we obtain at the critical point  $\frac{\partial v_x}{\partial x} = 0$ . Thus, using Expression (3) for viscous flow around obstacles one should always obtain  $P_{cr} = \infty$ . Davies and Peetz in their paper obtained finite values of  $P_{cr}$ , but they did so only because they used approximated expressions for the velocity components of the stream which do not exactly satisfy the boundary conditions of viscous flow around bodies. The values of  $P_{cr}$  determined by these authors have, thus, no real meaning and completely determined by the extent to which the approximate velocity gradient along the axial line deviates at the critical point from its exact value of zero.

Real (finite) values of  $P_{cr}$  in the case of viscous flow around bodies can be obtained by numerical integration of Eqs. (2). In order to do this it is necessary to know  $v_1$  as a function of the coordinates. Expressions for the velocity components of the stream in the case of viscous flow around a circular stationary cylinder of infinite length situated with its axis perpendicular to the direction of the stream, applicable at any distance from the cylinder, may be obtained from Oseen's equations [3]:

$$v_x = \frac{\partial \varphi}{\partial x} + \frac{1}{2k} \frac{\partial \chi}{\partial x} - \chi, \quad v_y = \frac{\partial \varphi}{\partial y} + \frac{1}{2k} \frac{\partial \chi}{\partial y}, \quad (4)$$

where

$$\varphi = \sum_{n=0}^{\infty} A_n \frac{\partial^n \ln r}{\partial x^n}, \quad \chi = -v_0 + e^{\lambda x} \sum_{n=0}^{\infty} B_n \frac{\partial^n K_0(kr)}{\partial x^n},$$

$K_0$  is the Bessel function to an imaginary argument,  $k = \frac{v_0 \gamma_2}{2\eta}$ ,  $\gamma_2$  is the density of the medium and  $\underline{r}$  the radius vector expressed in terms of polar coordinates. Since the constants  $A_n$  contain terms in  $ka$  to the power of  $(n-1)$  and constants  $B_n$  contain such terms to the power of  $n$ , it follows that at low Reynolds numbers,  $Re = 4ka$ , we may limit ourselves to taking into account only the first few terms of the expansions of  $\varphi$  and  $\chi$  in series. If in the expressions for  $v_1$  we neglect terms containing powers of  $ka$  higher than the first, it suffices to take into account only three terms in the expansion of  $\varphi$  and three terms in the expansion of  $\chi$  (actually, two terms in the expansion of  $\chi$  are sufficient, because on neglecting terms in  $k^2 a^2$  the constants  $A_2$  and  $B_2$  enter into expressions for  $v_1$  in the form of the linear combination  $A_2 - \frac{B_2}{2k} = A_2^0$ ). If we now substitute the expressions thus obtained for  $\varphi$  and  $\chi$  into Eqs. (4), neglect terms containing powers of  $ka$  higher than the first, and determine the constants  $A_0$ ,  $A_1$ ,  $A_2^0$ ,  $B_0$  and  $B_1$  from the boundary conditions  $v_x = v_y = 0$  for  $r = a$ , by equating terms with different powers of  $x$  and  $y$  to zero, we obtain

$$\begin{aligned} v_x^0 &= v_0 - \frac{2v_0}{1+2K_0} \left\{ e^{\lambda x} K_0(kr) + \left( e^{\lambda x} K_1(kr) - \frac{1}{kr} \right) \times \right. \\ &\times \left[ \frac{x}{r} + \frac{ka^2}{r} \left( \frac{1}{4} + K_0 \right) \left( 1 - 2 \frac{x^2}{r^2} \right) \right] + \frac{1}{2} \frac{a^2}{r^3} - \frac{a^2 x^2}{r^4} - \frac{3ka^4 x K_0}{2r^4} + \frac{2ka^4 x^3 K_0}{r^6} \Big\}, \\ v_y &= \frac{2v_0}{1+2K_0} \left\{ \left( e^{\lambda x} K_1(kr) - \frac{1}{kr} \right) \left[ \frac{2ka^2 xy}{r^3} \left( \frac{1}{4} + K_0 \right) - \frac{y}{r} \right] + \right. \\ &+ \frac{a^2 xy}{r^4} - \frac{ka^2 y}{r^3} \left( \frac{1}{4} + K_0 \right) + \frac{ka^4 y K_0}{2r^4} - \frac{2ka^4 x^2 y K_0}{r^6} \Big\}. \end{aligned} \quad (5)$$



( $K_0(ka)$  is henceforth being denoted by  $K_0$ ). On neglecting terms with first powers of  $ka$  and  $kr$  in Eqs. (5) we obtain the well-known expressions due to Lamb.

Expressions (5) differ in terms of the first degree with respect to  $ka$  from those obtained by Davies [4] and used by him [2, 5] to calculate  $\epsilon$  as a function of  $P$  for a Reynolds number of  $Re = 0.2$ . When calculating  $v_x$  and  $v_y$  by means of Eqs. (4) Davies used five terms in the expansion of  $\varphi$  and only one term in the expansion of  $\chi$ . In order to determine six constants he obtained, from boundary conditions, seven incompatible equations and was able to calculate the values of the constants and satisfy the boundary conditions only by neglecting - without sufficient reasons - a number of terms. For this reason the expressions obtained by Davies for  $v_i$  do not satisfy Eqs. (4) with respect to terms in  $ka$ .

In order to determine  $P_{cr}$  it is not absolutely necessary to calculate  $\epsilon$  as a function of  $P$ ; it is sufficient to consider the motion of the aerosol particle along the axial flow line of the stream and to determine for what minimum value of  $P = P_{cr}$  the particle will just reach the surface of the obstacle.

In the following we shall denote the dimensionless velocities of the stream and of the particle moving along the axis, respectively, by the letters  $V$  and  $U$  without suffixes. Using this notation the equation of motion of the aerosol particle along the central axis of the stream will have the form

$$P \frac{dU(x)}{d\tau} = V(x) - U(x). \quad (6)$$

The problem of determining  $P_{cr}$  thus reduces to the determination of the minimum value of  $P$  for which  $U > 0$  ( $U - V > 0$ ) at the surface of the obstacle, i. e., at  $X = -1$ .

One of the most accurate and amenable methods of numerical integration of differential equations is the method due to Adams [6]. In order to be able to apply this method in our case let us first transform Eq. (6) into the form  $PU \frac{dU}{dX} = V - U$  by means of the relation  $U dr = dX$ , and hence, putting  $h = -\frac{1}{X}$ , into

$$\frac{dU}{dh} = \frac{V - U}{PUh^2}. \quad (7)$$

To determine  $P_{cr}$  it is necessary to use this equation to calculate values of  $U$  at different values of  $P$  when  $h = 1$ , the initial condition being  $U = 1$  when  $h = 0$ .

The dependence of  $V$  on  $h$  in the case of the oncoming stream, derived from (5), is given by the expression (where  $r = -x = a/h$ ):

$$V = 1 - \frac{2}{1 + 2K_0} \left\{ e^{-hah} K_0(ka/h) - \left( e^{-hah} K_1(ka/h) - \frac{h}{ka} \right) \times \right. \\ \left. \times \left( 1 + \frac{1}{4} hka + hkaK_0 \right) - \frac{1}{2} h^2 - \frac{1}{2} h^3 kaK_0 \right\}. \quad (8)$$

In order to carry out the numerical integration of Eq. (7) by the method of Adams it is necessary to obtain by some method the first three or four values of  $U$  for small and equal intervals  $\Delta h$ . For this reason Eq. (7) was first integrated for small values of  $h$  ( $V = 1 - \frac{2h}{ka(1 + 2K_0)} = 1 - Ch$ ) by the method of indeterminate coefficients by expanding  $U$  into the series  $U = 1 + b_1 h + b_2 h^2 + b_3 h^3 + \dots$ . On substituting these expressions for  $V$  and  $U$  into Eq. (7) and equating the coefficients of equal powers of  $h$  we obtain

$$U = 1 - Ch + CP h^2 - CP(C + 2P) h^3 + 6CP^2(C + P) h^4 - \dots \quad (9)$$

Values of  $P_{cr}$  were determined for Reynolds number  $Re = 4ka = 0.1$ . First, values of  $U$  were calculated for  $h \leq 85 \cdot 10^{-4}$ . Then, using Adams' method, values of  $U$  were calculated for values of  $h > 85 \cdot 10^{-4}$  at intervals  $\Delta h$  which were at first equal to  $2.5 \cdot 10^{-4}$  and were subsequently increased progressively to  $h = 4 \cdot 10^{-2}$ . The intervals were so chosen as to secure a sufficient degree of accuracy in the values of  $\Delta h \frac{dU}{dh}$  and to be able to

limit ourselves to the consideration of second (and only very rarely to third) order differences of this quantity. The entire interval from  $h = 85 \cdot 10^{-4}$  to  $h = 1$  was divided into 94 intervals. Values of  $V$  and  $U$  were calculated to the fourth decimal place. In calculating  $V$  we have used eight-figure tables of functions  $K_0$  and  $K_1$  with argument increments of 0.001 [7]. For intermediate values of arguments linear, and where necessary parabolic interpolation was applied. Values of  $U$  were calculated for a number of values of  $P$ . A critical value of  $P = 4.3 \pm 0.1$  was obtained for Reynolds' number  $Re = 0.1$ ; above this value  $U - V > 0$  when  $h = 1$  (in the case of potential flow around a cylinder,  $P_{cr} = 1/8$  [1, 8]).

In a similar manner the value of  $P_{cr}$  was calculated for viscous flow around a sphere, following Oseen's method. In this case the following expressions are obtained for the velocity components of the stream (the degree of accuracy being carried to terms of the first power of  $ka$ ):

$$v_x = v_0 - \frac{3v_0}{4-3ka} \frac{a}{r} \left[ e^{k(x-r)} \left( 1 + \frac{x}{r} + \frac{x}{kr^2} + \frac{a^2}{r^3} - 3 \frac{a^2 x^2}{r^4} \right) - \frac{x}{kr^2} - \frac{2a^2}{3r^2} + 2 \frac{a^2 x^2}{r^4} + \frac{ka^2}{r} \left( 1 - \frac{3x^2}{r^2} - \frac{3a^2 x}{2r^3} + \frac{5a^2 x^3}{2r^4} \right) \right], \quad (10)$$

$$v_p = \frac{3v_0}{4-3ka} \frac{ap}{r^2} \left[ e^{k(x-r)} \left( 3 \frac{a^2 x}{r^3} - \frac{1}{kr} - 1 \right) + \frac{1}{kr} - 2 \frac{a^2 x}{r^3} - \frac{ka^2}{r} \left( 1 - \frac{3x}{r} - \frac{a^2}{2r^2} + \frac{5a^2 x^2}{2r^4} \right) \right],$$

where  $x$  and  $p$  are cylindrical coordinates, and  $r$  is the spherical radius vector. As  $ka$  and  $kr$  both tend towards zero ( $ka \rightarrow 0$  and  $kr \rightarrow 0$ ) these expressions assume the form valid for Stokesian flow around bodies. A value of  $P_{cr} = 1.15 \pm 0.01$  was calculated for  $Re = 0.1$ .

Finally, a similar calculation was carried out for the case of Stokes' flow around a sphere. A value of  $P_{cr} = 1.21 \pm 0.01$  was obtained which is in full agreement with the value of  $P_{cr} = 1.214$  obtained by Langmuir [8] by means of the differential analyzer (in the case of potential flow around a sphere,  $P_{cr} = 1/12$  [1, 8]).

It must be stressed that the notion of a critical value of  $P$  is linked only with that part of the sedimentation process which is governed by the inertia of the particles alone. As will be seen from the above, the conclusion that  $\epsilon = 0$  when  $P < P_{cr}$  is reached only on the assumption that a particle becomes adsorbed when its center of gravity reaches the surface of the obstacle. Actually, adsorption takes place when the particle approaches the surface to within a distance equal to its radius. If this circumstance is taken into account, it will be seen that when  $P < P_{cr}$  adsorption will also take place by virtue of pure adhesion. In the case of viscous flow around a cylinder and for small values of  $\epsilon$  the coefficient of adsorption due to adhesion alone is given by  $\epsilon = \frac{2}{1+2K_0} \times \frac{R^2}{a^2}$ . Thus, the effect of the dimensions of the particles on the coefficient of adsorption will be small only when  $R \ll a$ . Strictly speaking, the latter condition would also be expected to prevail when the reaction of the particle on the velocity field of the stream circumflowing the obstacle is negligibly small. Since  $P = \frac{R^2 \gamma_1 Re}{9a^2 \gamma_2}$ , it follows that  $\frac{R^2}{a^2} > \frac{9\gamma_2 P_{cr}}{\gamma_1 Re}$  when  $P > P_{cr}$ . Hence, at small Reynolds numbers the conditions  $P > P_{cr}$  and  $R \ll a$  cannot be fulfilled simultaneously. For  $Re = 0.1$ ,  $P_{cr} = 4.3$  and  $\gamma_2 = 1.2 \cdot 10^{-3}$ , condition  $P > P_{cr}$  necessitates  $\frac{R^2}{a^2} > \frac{0.46}{\gamma_1}$ , i. e., condition  $R \ll a$  can be realized only in the case of aerosols of certain metals ( $\gamma_1 \gg 1$ ).

#### LITERATURE CITED

- [1] L. M. Levin, Proc. Acad. Sci. USSR 91, 1329 (1953).
- [2] C. N. Davies and C. V. Peet, Proc. Roy. Soc. A 234, 269 (1956).

- [3] N. E. Kochin, I. A. Kibel and N. V. Roze, *Theoretical Hydromechanics*, Vol. 2, Ch. 2, Par. 25-26 (Moscow-Leningrad, 1948).\*
- [4] C. N. Davies, *Proc. Phys. Soc.* 63, 268 (1950).
- [5] C. N. Davies, *Proc. Inst. Mech. Eng.*, London, 1, 185 (1952).
- [6] A. N. Krylov, *Lectures on Approximate Calculations*, Par. 93-95 (Moscow-Leningrad, 1950).\*
- [7] *Tables of Values of Bessel Functions for a Complex Argument* (Acad. Sci. USSR Press, 1950).\*
- [8] I. Langmuir, *J. Meteorol.* 5, 175 (1948), reprinted in *Physics of Sedimentation*, 1951, Foreign Literature Press [Russian translation].

Received April 3, 1957

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\* In Russian.

ON THE ROLE OF ADSORPTION KINETICS IN WETTING PROCESSES OF  
DUST PARTICLES BY DROPLETS OF SOLUTIONS OF  
SURFACE-ACTIVE AGENTS

S. A. Nikitina and A. B. Taubman

(Presented by Academician P. A. Rebinder, April 13, 1957)

In the course of investigations on the dust-absorbing action of sprays of solutions of surface-active agents of the semi-colloidal type, for example of wetting agents DB and OP-10, we have found considerable differences in their dust-absorbing ability, in spite of the close resemblance of their chemical composition and molecular structure [1]. These differences were also found in the case of solutions having practically the same static surface tension equal to the lower limiting value of 30-35 ergs/cm<sup>2</sup>.

In contrast to solutions of molecularly dissolved surface-active substances — organic acids, alcohols, etc. — in which adsorption equilibrium is attained within fractions of a second [2], in the case of micellar colloidal solutions of soap-like wetting agents the attainment of adsorption equilibrium corresponding to static surface tension requires considerable time [3].

Now, the absorption of dust particles by water droplets is brought about under kinetic conditions during their short-lasting collisions (contact); in some cases such collisions result in actual absorption of the dust particles by the droplets, while in others such absorption fails to take place as a result of the rebounding of the droplets from the dust particles [4]. Since the probability of absorption of a dust particle as a result of its being wetted by the solution increases with the extent of the lowering of surface tension of the latter prior to the collision, it is obvious that the efficiency of dust absorption will depend in considerable measure on the extent to which the adsorption layer will have formed by that time, and, consequently, on the relative lowering of the dynamic surface tension ( $\sigma_d$ ), that is, on the extent to which the latter will have approached the value of static surface tension ( $\sigma_s$ ) corresponding to the equilibrium state of the surface layer of the droplet of the solution at the given concentration.

From the above it follows that the lowering of static surface tension of solutions of surface-active substances does not characterize their true wetting properties under actual conditions of dust absorption:  $\sigma_d$  may vary from values close to the surface tension of pure water ( $\sigma_0$ ) to the minimum value,  $\sigma_s$ .

It is obvious that these differences which arise from the particular properties of solutions of colloidal wetting agents, might be detected in the course of investigations of their surface activity under conditions of varying duration of the interface solution-air ( $\tau$ ); under conditions obtaining in actual dust-collecting practice the duration of this interface may vary within wide limits. For this reason, and in view of the applicability of the usual methods of determination, we have measured  $\sigma_d$  of the solutions by droplet counts for  $\tau = 2$  sec, and  $\sigma_s$  by the pendant drop method [5] for  $\tau = 2$  min; under our conditions these periods were always sufficient for adsorption equilibrium to be attained.

From Fig. 1 it will be seen that in solutions of wetting agent DB and of Aerosol OT adsorption equilibrium is attained relatively rapidly and both isotherms — of dynamic and static surface tension,  $\sigma_d(C)$  and  $\sigma_s(C)$  — approach each other rapidly with increasing concentration and practically coincide at a certain value of the latter. In the case of wetting agent DB this concentration is equal to 0.08-0.1% and in the case of Aerosol OT to 0.22-0.25%, which is in agreement with the critical micelle concentration (CMC) reported in the literature [6].

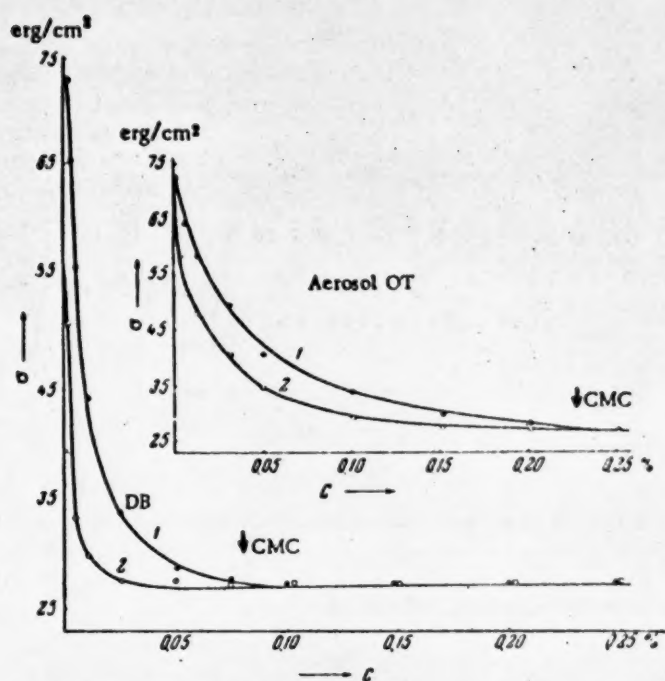


Fig. 1. Isotherms of dynamic ( $\sigma_d$ ) and static ( $\sigma_s$ ) surface tension of solutions of wetting agent DB and Aerosol OT. 1)  $\sigma_d$  for  $\tau = 2$  sec; 2)  $\sigma_s$  for  $\tau = 2$  min.

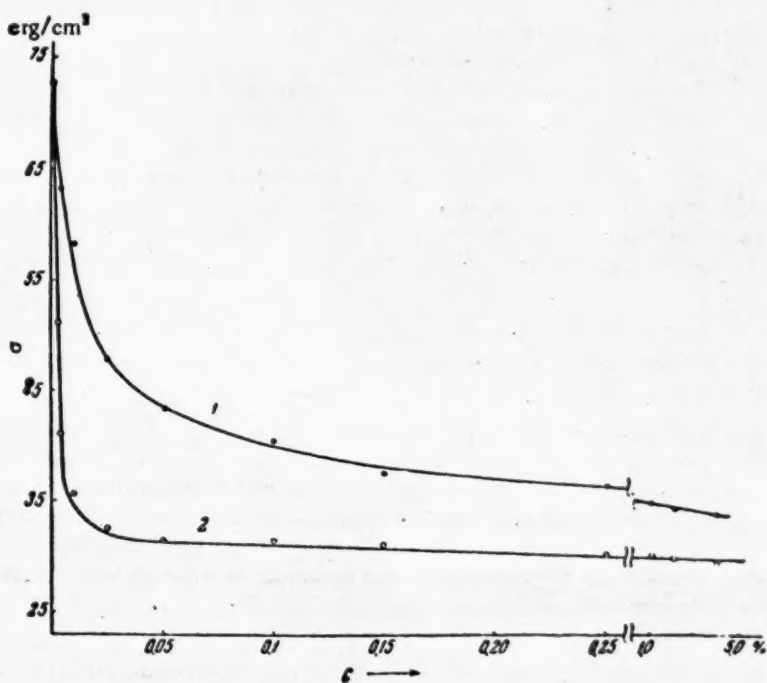


Fig. 2. Isotherms of dynamic ( $\sigma_d$ ) and static ( $\sigma_s$ ) surface tension of solutions of wetting agent OP-10. 1)  $\sigma_d$  for  $\tau = 2$  sec; 2)  $\sigma_s$  for  $\tau = 2$  min.



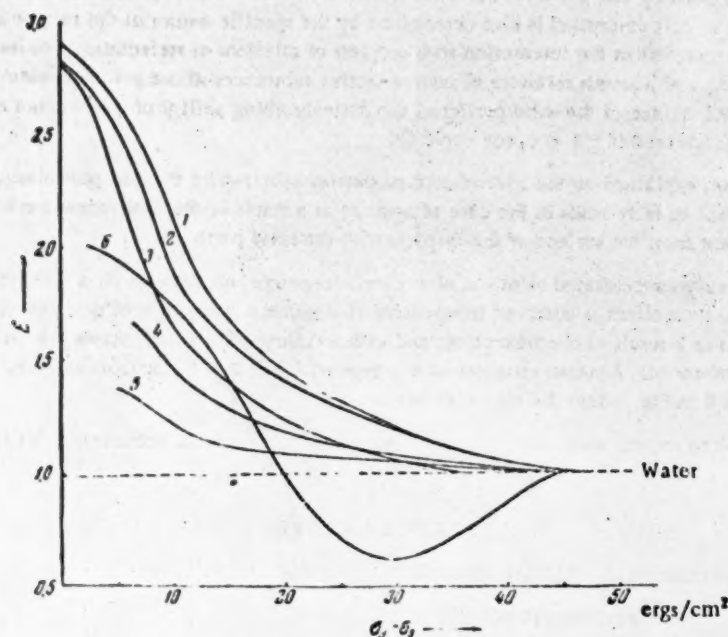


Fig. 3. Dependence of the efficiency of wetting ( $E$ ) of quartz dust on  $\Delta\sigma = \sigma_d - \sigma_s$  for different surface-active substances. 1) Wetting agent DB, 2) Aerosol OT, 3) purified alkylaryl sulfonate, 4) wetting agent OP-10, 5) sulfonated alcohol, 6) dodecylamine acetate.

It is well known that at this and higher concentrations the formation of the equilibrium (saturated) adsorption layer is complete within a very short time, namely, within periods of the order of less than tenths of a second [7]. Thus, the simultaneous determination of  $\sigma_d$  and  $\sigma_s$  at the concentration at which both values are practically identical, may be regarded as a new method of determination of the CMC.

A different relationship is observed in the case of surface tension isotherms of solutions of wetting agent OP-10 (Fig. 2). In this case the difference between  $\sigma_d$  and  $\sigma_s$  is large and, what is important, is also maintained at higher concentrations (up to 4%), namely, at concentrations 100 times higher than that at which the constant value of  $\sigma_s \sim 30$  ergs/cm<sup>2</sup> is attained. This clearly indicates the slow rate of formation of adsorption layers in solutions of surface active agents of this type; as a result, sufficiently low values of  $\sigma_d$  cannot be attained at any concentrations under conditions when the duration of the freshly formed interface solution-air is short. The reason for this lies in the fact that the wetting agents in question, unlike wetting agents DB and Aerosol OT, constitute a molecular mixture of components of different molecular weights (containing hydrocarbon chains of varying length and structure) as a result of which formation of micelles in their solutions proceeds slowly over a wide range of concentrations [8]. This, in turn, leads to the retardation of the kinetics of formation of adsorption layers and to a reduction in the efficiency of their dust-absorbing activity.

On the other hand, in the case of solutions of wetting agents in which micelle formation is completed at the point corresponding to the meeting of the isotherms  $\sigma_d(C)$  and  $\sigma_s(C)$  and to the critical micelle concentration (CMC), when  $\sigma_d - \sigma_s \approx 0$ , the efficiency of collisions between dust particles and droplets under kinetic conditions will be greatest.

The dependence of the relative efficiency ( $E$ ) of wetting by solutions of surface-active agents [1], as compared with water, on the difference  $\sigma_d - \sigma_s$  is represented graphically in Fig. 3 from which it will be seen that wetting agents DB and Aerosol OT do, in fact, possess the greatest efficiency in wetting. The dependence of  $E$  on  $\sigma_d - \sigma_s$  has a meaning only when we are comparing solutions having practically identical and sufficiently



low values of static surface tension,  $\sigma_s$ . In general one would expect that the dependence of  $E$  on  $\sigma_d$  or on  $\sigma_d - \sigma_s$  would be expressed by one universal curve for different surface-active agents. However, this is not the case since the process of dust absorption is also determined by the specific nature of the surface of the dust particles which becomes manifest in the interaction with droplets of solutions of surfactants. We have, in fact, shown [4] that in the case of aqueous solutions of surface-active substances whose polar groups may become chemically fixed on the surface of the solid particles, the dust-absorbing ability of water is not enhanced ( $E > 1$ ), but, on the contrary, is lowered ( $E - 1 < 0$ , see curve 6).

This is, of course, explained by the hydrophobic properties acquired by the dust particles (due to amines in the case of quartz and to fatty acids in the case of apatite) as a result of the slow migration of molecules of the surface-active agent from the surface of the droplets onto the solid particles.

In the case of fairly concentrated solutions of any surface-active substances with a sufficiently low dynamic surface tension  $\sigma_d$ , no such effect is observed irrespective of whether a given type of dust can or cannot acquire hydrophobic properties as a result of chemisorption, and with solutions of such surfactants the efficiency of dust absorption is always enhanced. Aqueous solutions of this type will wet any hydrophobic surface, and this explains the transition of curve 6 in Fig. 3 into the region of wetting.

The authors wish to express their sincere gratitude to Academician P. A. Rebinder for his interest in this work and for valuable advice.

#### LITERATURE CITED

- [1] A. B. Taubman and S. A. Nikitina, Proc. Acad. Sci. USSR 110, 4 (1956).
- [2] C. C. Addison, J. Chem. Soc. 1944, 477.
- [3] A. Schwarz and D. Perry, Surface-Active Substances (Foreign Literature Press, 1953) [Russian translation].
- [4] A. B. Taubman and S. A. Nikitina, Proc. Acad. Sci. USSR 110, 5 (1956).
- [5] M. M. Kusakov, N. M. Lubman and A. Yu. Koshevnik, Trans. Inst. Petroleum, Acad. Sci. USSR 2, 53 (1952).
- [6] A. P. Brady and D. I. Salley, J. Am. Chem. Soc. 70, 914 (1948).
- [7] N. K. Adam and H. L. Shute, Trans. Farad. Soc. 34, 758 (1938); G. C. Nutting, F. A. Long and N. B. Harkins, J. Am. Chem. Soc. 62, 1496 (1940); 63, 84 (1941).
- [8] L. M. Kushner and W. D. Hubbard, J. Phys. Chem. 58, 12, 1163 (1954).

Received April 4, 1957

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# ON THE DEPENDENCE OF THE OXIDIZABILITY OF HYDROCARBONS IN THE LIQUID PHASE ON THEIR STRUCTURE

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(Presented by Academician N. N. Semenov, April 27, 1957)

On the basis of the general assumptions of the chain theory, N. N. Semenov [1, 11] arrived at the conclusion that the rate of oxidation of hydrocarbons would be determined by the strength of the weakest C—H bond in their molecules. In the present paper we are examining data on the oxidizability, in the liquid phase, of hydrocarbons with 7-10 carbon atoms found in the literature [2, 4, 5] and also those obtained by us [6] (see also Fig. 1), and we shall compare these data with those given by Voevodsky [3] and Semenov [11] relating to the C—H bond strengths in these hydrocarbons (Table 1).

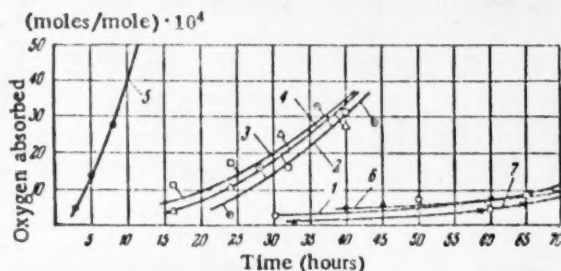



Fig. 1. Oxidation of paraffinic hydrocarbons and of toluene ( $t_0 = 100^\circ$ ;  $p_0 = 1$  atmos. abs.). Oxygen absorption (axis of ordinates) in moles/mole  $\cdot 10^4$ . 1) n-Heptane, 2) n-octane, 3) n-nonane, 4) n-decane, 5) 2,6-dimethylpentane, 6) 2,2,4-trimethylpentane, 7) toluene.

In accordance with the views held by representatives of the Hinshelwood school [7], during low-temperature oxidation of paraffinic hydrocarbons molecular oxygen attacks, first of all, the center groups of the chain, which indicates that the weakest C—H bonds are situated at the center of the hydrocarbon molecule. A similar conclusion is reached from an analysis of the equations deduced by V. V. Voevodsky [3].

The structures of the hydroperoxides of 2-methylhexane, 2,2,4-trimethylpentane and 2,7-dimethyloctane indicate that experimental data [2] and the existing theoretical considerations [3, 7] with reference to the location of the weakest C—H bonds in the molecules of these hydrocarbons lead to the same conclusion. No such agreement between theory and experiment exists in the case of n-heptane; contrary to the views frequently expressed in the literature, oxidation of a straight paraffinic chain does not begin at the first [8] or the central [9, 10], but at the second carbon atom of the chain [2]. The structure of hydroperoxides of normal octane, nonane, and decane is, unfortunately, so far unknown.

TABLE 1

Bond Rupture Energies of the Weaker C—H Bonds of Some Hydrocarbons and Their Oxidizability in the Liquid Phase

Name of hydrocarbon	Location of the weakest C—H bond (asterisk) and direction of the primary attack by oxygen (arrows) according to K. I. Ivanov	Rupture energy of the weakest C—H bond, kcal/mole	Oxidizability of the hydrocarbon in the liquid phase
Normal Paraffins			
n-Heptane	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{*}{\text{CH}}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ $\uparrow$	86.64 <sup>1,2</sup>	Rate of oxidation the same as in the case of 2,2,4-trimethylpentane and toluene [2, 4, 6], but considerably slower than in the case of normal octane, nonane and decane [6]
n-Octane	$\text{CH}_3(\text{CH}_2)_2-\overset{*}{\text{CH}}_2-\overset{*}{\text{CH}}_2(\text{CH}_2)_2\text{CH}_3$	86.35 <sup>2</sup>	Undergoes oxidation much more vigorously than n-heptane, 2,2,4-trimethylpentane or toluene, and at about the same rate as normal nonane and decane [6]
n-Nonane	$\text{CH}_3(\text{CH}_2)_3\overset{*}{\text{CH}}_2-(\text{CH}_2)_3\text{CH}_3$	86.08 <sup>2</sup>	Undergoes oxidation much more vigorously than n-heptane, and at about the same rate as n-octane and n-decane [6]
n-Decane	$\text{CH}_3(\text{CH}_2)_3\overset{*}{\text{CH}}_2\overset{*}{\text{CH}}_2-(\text{CH}_2)_3\text{CH}_3$	85.92 <sup>2</sup>	Undergoes oxidation much more vigorously than n-heptane and at about the same rate as n-octane and n-decane [6]
Isoparaffins			
2-Methylhexane	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\overset{*}{\text{CH}}(\text{CH}_2)_3\text{CH}_3 \\ \uparrow \end{array}$	85.95 <sup>2</sup>	Undergoes oxidation with considerably greater ease than n-heptane and 2,2,4-trimethylpentane [4]
2,2,4-Trimethylpentane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\overset{*}{\text{C}}-\text{CH}_2-\overset{*}{\text{CH}}-\text{CH}_3 \\   \quad \uparrow \\ \text{CH}_3 \end{array}$	84.54 <sup>2</sup>	Undergoes oxidation with equal ease as n-heptane and toluene [2, 4, 6]
2,6-Dimethylheptane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\overset{*}{\text{CH}}(\text{CH}_2)_3\overset{*}{\text{CH}}-\text{CH}_3 \end{array}$	84.16 <sup>2</sup>	Undergoes oxidation much more vigorously than n-nonane [6]
2,7-Dimethyloctane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\overset{*}{\text{CH}}(\text{CH}_2)_4\overset{*}{\text{CH}}-\text{CH}_3 \end{array}$	84.06 <sup>2</sup>	Undergoes oxidation more vigorously than n-decane [5]
Aromatic Hydrocarbons			
Benzene		99 <sup>3</sup>	Practically no oxidation takes place in the liquid phase [2, 5]
Toluene	$\text{H}_2\overset{*}{\text{C}}-\text{H}$ 	77.5 <sup>3</sup>	Undergoes oxidation with equal ease as n-heptane and 2,2,4-trimethylpentane [2, 4, 6]

Notes. 1. The bond rupture energy given refers to the C—H bond marked with an asterisk; the rupture energy of the C—H bond at the point of location of the peroxide group is equal to 88.9 kcal/mole. 2. Calculated from Voevodsky's equations [3]. 3. Experimental values [11].

The C—H bond rupture energies for the weaker bonds in the case of normal paraffins with 7-10 carbon atoms calculated by means of the Voevodsky equations [3] are very close to each other. However, while n-octane, n-nonane and n-decane do, in fact, undergo oxidation in the liquid phase with almost equal ease (see Fig. 1), n-heptane differs in this respect in that it exhibits marked resistance to oxidation.

The iso-paraffinic hydrocarbons which do not contain a quaternary carbon atom are characterized by the presence of C—H bonds which are weaker than those in the corresponding normal paraffins. The former hydrocarbons do, in fact, undergo oxidation in the liquid phase with considerably greater ease than the latter (see 2-methylheptane and n-heptane, 2,6-dimethylheptane and n-nonane, 2,7-dimethyloctane and n-decane).

However, the very high resistance of paraffins containing a quaternary carbon atom (trimethylpentanes) to oxidation in the liquid phase [4, 6] is in direct contrast to the C—H bond strength characteristics of these hydrocarbons as calculated from Voevodsky's equations [3]; these equations do not take into account the "screening" effect due to the quaternary carbon atom in iso-paraffinic hydrocarbons.

As has been pointed out, in the case of toluene and benzene the bond rupture energy of the weakest C—H bond has been determined experimentally [11]; in the case of toluene the value obtained is considerably less than those given here for the bond rupture energy of the weakest C—H bonds in any paraffinic hydrocarbons. In view of this it might be expected that toluene would undergo oxidation with considerably greater ease than the paraffins investigated. However, experimental data [2, 6] (see Fig. 1) indicate that not only does toluene not undergo oxidation with greater vigor than the paraffins, but that it is, in fact, considerably more resistant to oxidation in the liquid phase than are n-octane, n-nonane and n-decane and approximately equal in this respect to the most stable of the paraffins investigated, namely, n-heptane and 2,2,4-trimethylpentane.

On the other hand, in the case of benzene the high value of the C—H bond rupture energy corresponds to the exceptionally great resistance of this compound to oxidation in the liquid phase.

We are thus led to the conclusion that on the basis of the available experimental facts it is impossible to discover any relationship between the bond rupture energy of the weakest C—H bonds in molecules of hydrocarbons and their relative ease of oxidation in the liquid phase.

#### LITERATURE CITED

- [1] N. N. Semenov, Problems of Oxidation of Hydrocarbons (Acad. Sci. USSR Press, 1954), p. 13.\*
- [2] K. I. Ivanov, Intermediate Products and Intermediate Reactions in the Auto-Oxidation of Hydrocarbons (Moscow, 1949).\*
- [3] V. V. Voevodsky, Proc. Acad. Sci. USSR 79, 3, 455 (1951).
- [4] K. I. Ivanov, V. P. Zhakhovskaya and V. K. Savinova, Paper presented at the All-Union Symposium on the Oxidation of Hydrocarbons (Acad. Sci. USSR Press, 1951), pp. 15, 17.\*
- [5] N. I. Chernozhukov and S. E. Krein, The Oxidizability of Mineral Oils (Moscow, 1955).\*
- [6] I. V. Rozhkov and E. N. Kornilova, Chemistry and Technology of Fuels, No. 12 (1956).
- [7] C. Cullis, C. Hinshelwood and M. Mulcohy, Proc. Roy. Soc. (London) A 196, 160 (1949).
- [8] J. Pope, F. Dykstra and G. Edgar, J. Am. Chem. Soc. 51, 1875, 2203, 2213 (1929).
- [9] A. Grün, Ber. 53, 955 (1950).
- [10] M. Mulcohy, Trans. Farad. Soc. 45, 537 (1949).
- [11] N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity (Acad. Sci. USSR Press, 1954).\*

Received March 9, 1957

\* In Russian.



# ANODIC POLARIZABILITY OF ALLOYS OF Al WITH ALKALINE EARTH ELEMENTS IN NEUTRAL ELECTROLYTES

A. L. Seifer

(Presented by Academician I. I. Chernyaev, May 23, 1957)

It has been suggested [1] that the increase (in the direction of positive values) of electrode potentials of Al-Ca alloys in sea-water is connected with the decomposition of the oxide film on the surface of the alloy by the products of corrosion of the intermetallic compound  $Al_4Ca$ . However, it is also necessary to take into account the fact that in sea-water which contains a certain amount of sulfate ions, there may be taking place a simultaneous formation of a film of sparingly soluble calcium sulfate on the surface of the aluminum-calcium alloys.

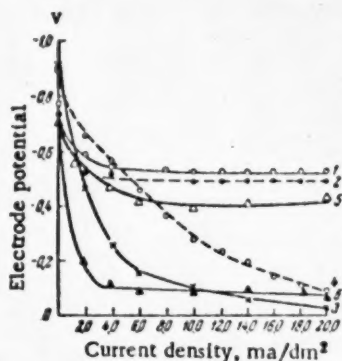


Fig. 1. Anodic polarizability of Al-Ca alloys.  
1) Al + 3.93% Ca in 0.5 N NaCl, 2) Al + 12.26% Ca in 0.5 N NaCl, 3) Al + 3.93% Ca in 0.5 N  $Na_2SO_4$ , 4) Al + 12.26% Ca in 0.5 N  $Na_2SO_4$ , 5) technically pure Al in 0.5 N NaCl, 6) Al (techn. purity) in 0.5 N  $Na_2SO_4$ .

NaCl and  $Na_2SO_4$  at polarizing current densities of up to 20 milliamp/dm<sup>2</sup>. The results are given in Table 1 and in Figs. 1-3.

As will be seen from the graphs and the table, the characteristics of anodic polarizability of the alloys described depends both on the nature of the electrolyte and the nature of the added alkaline earth element.

In the 0.5 N solution of NaCl the predominant process will be the dissolution of the oxide film on the surface of the alloy. The ease with which the film can be decomposed, which is determined by the relative shift of the electrode potential in the direction of less negative values, increases with the nature of the added alkaline earth element in the order Ca-Sr-Ba and also with the amount added. As the secondary dissociation constant of the hydroxides increases from 0.03 for  $Ca(OH)_2$  to 0.23 for  $Ba(OH)_2$  [5] and with increasing total amount of hydroxides formed (as a result of the interaction of the intermetallic compounds  $Al_4M$  with water), in proportion

It was therefore deemed of interest to investigate the anodic polarizability of alloys of Al with Ca, Sr and Ba not only in sea-water, but also in solutions of sodium sulfate and sodium chloride - "limiting models" of sea-water - since the nature of anodic polarization in these electrolytes may throw light on the nature of the processes leading to the formation or decomposition of protective films on the surface of the electrode. It may be mentioned that alloys of Al with Ca, Sr and Ba possess a structure similar to the intermetallic compound of the type  $Al_4M$  which is a component of the eutectic mixture [2-4].

Alloys of Al with Ca, Sr and Ba were prepared by dissolving the respective metals in molten aluminum of high purity under a layer of carnallite flux. The weight percentage composition of the alloys is given in Table 1. The content of Fe in the cast ingots did not exceed 0.03%.

The anodic polarizability of these alloys was examined in Caspian sea-water and in 0.5 N solution of

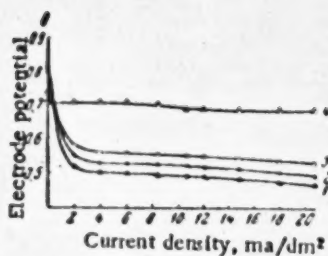


Fig. 2. Anodic polarizability of alloys of Al with Sr and Al with Ba in 0.5 N NaCl. 1) Al + 1.06% Sr, 2) Al + 4.69% Sr, 3) Al + 7.25% Sr, 4) Al + 94% Ba. [As in original - Publisher.]

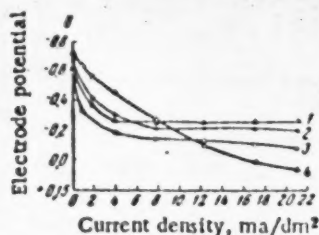


Fig. 3. Anodic polarizability of alloys of Al with Sr and Al with Ba in 0.5 N Na<sub>2</sub>SO<sub>4</sub>. 1) Al + 1.06% Sr, 2) Al + 4.69% Sr, 3) Al + 1.94% Ba.

the protective film, the formation on the surface of the alloy of an additional protective film of the sparingly soluble sulfates of elements of the Ca-subgroup. Since the solubility of the sulfates decreases in the order Ca-Sr-Ba, alloys of aluminum with Ba undergo polarization to a greater extent than is the case with alloys of Al with Sr and Ca. With increasing amount of the alkaline earth element added to the alloy the anodic polarizability increases due to an increase in the total amount of sulfates formed. This is clearly seen from the graphs in Figs. 2 and 3.

In Caspian sea-water the general lie of the curves is similar to that obtained for the 0.5 N solution of NaCl; however, in this case the electrode potentials are considerably less negative as a result of the formation on the electrode surface of a small amount of sparingly soluble sulfates.

Thus, during the anodic dissolution of alloys of aluminum with elements of the Ca-subgroup in sea-water two simultaneous processes are taking place, namely, dissolution of the oxide film by the action of hydroxyl ions and formation of a new film composed of sulfates. It is clear, however, that it is the lesser strength of the sulfate film as compared with the oxide film which is responsible for the close analogy between the polarizability of these alloys in sea-water and their polarizability in NaCl solutions.

#### LITERATURE CITED

- [1] I. N. Frantsevich and Z. P. Kamzolova, Proc. Acad. Sci. Ukr. SSR No. 1, 82 (1955).
- [2] H. Nowotny and H. Wesenberg, Zs. Metallkunde 31, 363 (1939).
- [3] H. Nowotny, A. Mohryheim and E. Wormnes, Zs. Metallkunde 32, 39 (1940).
- [4] E. Alberty and R. R. Andress, Zs. Metallkunde 27, 126 (1935).
- [5] B. V. Nekrasov, Textbook of General Chemistry, 9th Ed., 1952, p. 642.\*

Received December 12, 1956

\* In Russian.

TABLE 1

Electrode Potentials of Alloys of Al with Ca, Sr and Ba in Caspian Sea-Water at Different Anodic Polarizing Current Densities (referred to the normal electrode, in volts)

Composition of alloy	Anode density, ma/dm <sup>2</sup>		
	0	10	20
Al, techn. purity	-0.58	-0.45	-0.42
Al+3.93% Ca	-0.59	-0.47	-0.44
Al+6.85% Ca	-0.49	-0.45	-0.43
Al+12.26% Ca	-0.62	-0.48	-0.45
Al+1.06% Sr	-0.58	-0.45	-0.43
Al+4.69% Sr	-0.65	-0.47	-0.45
Al+7.25% Sr	-0.64	-0.55	-0.52
Al+1.94% Ba	-0.67	-0.66	-0.66

Note. Temperature of the electrolyte solution = 20°. The surface of the electrode was exposed to air prior to immersion in the electrolyte.

to the amount of the alkaline earth element added, there is an increase in the amount of hydroxyl ions present in the electrode space of the alloy undergoing anodic polarization. The hydroxyl ions present in the anode space serve mainly to facilitate the dissolution of the oxide film on the surface of the alloy.

In 0.5 N solution of Na<sub>2</sub>SO<sub>4</sub> there proceeds, in the absence of the activating action of the chloride ion on



# A METHOD FOR THE DETERMINATION OF SPECIFIC SURFACES FROM THE ADSORPTION OF GASES IN THE MONOMOLECULAR REGION

M. G. Kaganer

(Presented by Academician M. M. Dubinin, June 4, 1957)

There exist several methods for the determination of the specific surfaces of adsorbents. Of these the most generally employed are the methods based on adsorption of gases. Included here are the methods of Brunauer, Emmett and Teller (BET), of Harkins and Jura (HJ) and of Gregg. This latter technique is only rarely employed; it has recently been shown [1] that it is not an independent method but ties up with the BET equation. The BET and the HJ methods are based on the measurement of polymolecular adsorption. Thus they do not give trustworthy values for the surface areas of finely porous adsorbents in general, and of many active gels in particular.

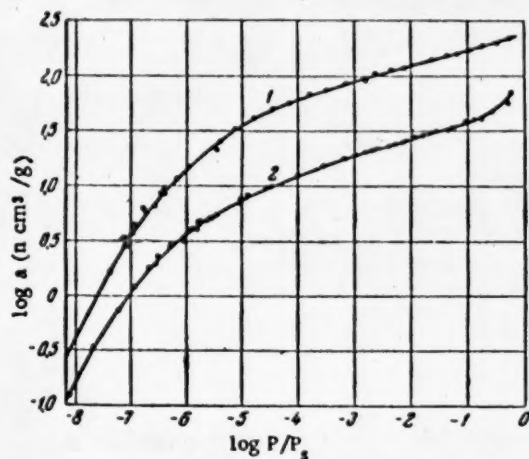


Fig. 1. Adsorption isotherms for nitrogen at 77.4°K and at pressures from  $1 \cdot 10^{-5}$  to  $4 \cdot 10^{-2}$  mm of Hg. 1) Silicagel, 2) aluminum oxide.

A new method, which is independent of those already existing, can be based on measurements in the region of monomolecular adsorption. We have determined the adsorption of nitrogen on specimens of silica-gel and aluminum oxide at 77.4°K and at  $p/p_s$  values ranging from  $1 \cdot 10^{-5}$  to 0.5. These measurements were carried out by the volumetric method. At pressures below  $1 \cdot 10^{-3}$  mm of Hg equilibrium was established in 15-25 hours. In the pressure determinations a correction was introduced for the thermomolecular effect [2]. Adsorption isotherms are presented in Fig. 1.

At small values of  $\Theta$ , the degree of surface coverage, the nonuniformity of the surface has a great effect on the form of an isotherm. The most active positions are usually covered at low values of  $p/p_s$ . At  $\Theta$  values of the order of several tenths there remain uncovered the relatively uniform portions of the surface which are characterized by an approximately constant heat of adsorption (see, for example, [3]). It can be supposed that measurements over this part of the monomolecular adsorption ( $\Theta > 0.2-0.3$ ) would be suitable for the determination of the surface area.

Over this range of  $\Theta$  values the data obtained by us is best described by the equation of M. M. Dubinin and L. V. Radushkevich [4]:

$$a = \frac{w_0}{v} \exp \left[ -B \frac{T^2}{\beta^2} \left( \log \frac{p_0}{p} \right)^2 \right]. \quad (1)$$

where  $w_0$  and  $B$  are constants characteristic of the adsorbent,  $v$  is the specific volume in the liquid phase of the substance whose vapors are being adsorbed and  $B$  is the affinity coefficient of the characteristic curves.

This equation can also be written in the following form:

$$\log a = C - D \left( \log \frac{p}{p_s} \right)^2 = C - D \left( \log \frac{p}{p_s} \right)^2, \quad (2)$$

where  $C = \log (w_0/v)$  and  $D = 0.43 BT^2/B^2$ . In the case of the adsorption of benzene on active charcoals, M. M. Dubinin, E. D. Zaverina and L. V. Radushkevich have established [5, 6] that  $\log a$  depends linearly on  $(\log p/p_s)^2$  at  $p/p_s$  values ranging from  $10^{-5}$ - $10^{-4}$  to 0.01-0.5.

Through the study of the data of Fig. 1, and of other published experimental results on adsorption at low  $\Theta$  values, we have been led to the conclusion that over a certain interval all adsorbents follow Eq. (2), the deviation of the points from a straight line at high  $p/p_s$  values being the greater the more coarsely porous the adsorbent.

TABLE 1

The Specific Surfaces of Adsorbents as Determined by Various Methods

No.	Specimen	S, m <sup>2</sup> /g			D	Source
		according to BET	according to HJ	from monomolecular adsorption		
1	Coked carbon	1550	—	1410	0.0172	[7]
2	Silica gel	674	—	644	0.0247	author
3	Silica gel K	440	430	422	0.0401	[8]
4	Aluminosilica gel	240	240	249	0.0463	[9]
5	Aluminum oxide	155	158	146	0.0281	author
6	Carbon black	80.4	88.7	83.1	0.0160	[10]
7	Bone charcoal	28.9	26.4	28.3	0.0297	[7]
8	Barium sulfate	9.7	9.65	9.6	0.0169	[11]

bent, i. e., the greater the value of  $n$ , the mean number of layers which can be adsorbed on the pore walls. For finely porous active carbons with  $n \approx 1$ , the value of  $w_0/v$  is equal to volume of gas,  $a_m$ , which is adsorbed in the monomolecular layer. When plotted in the coordinates of Eq. (2) the experimental points, in this instance, fall on a straight line which cuts the axis of ordinates at a point K with the ordinate  $C = \log a_m$ .

On the basis of what has been said it can be concluded that the value of  $a_m$  may be obtained for any adsorbent by extrapolating to the axis of ordinates ( $p/p_s = 1$ ) the linear portion of the isotherm plotted in the indicated coordinates. This amounts to assuming that Eq. (2) describes the adsorption of the first layer of molecules and that deviations at high  $p/p_s$  values result from adsorption in the second and in subsequent layers.

This supposition is fully confirmed by our own data and by the data of other investigators on the adsorption of nitrogen at low pressures. In Fig. 2 there are given isotherms for the adsorption of nitrogen at 77-78° K on eight different adsorbents with surface areas ranging from 10 to 1500 m<sup>2</sup>/g. In the coordinates of Eq. (2) all of these isotherms have linear sections at  $p/p_s$  values ranging from  $10^{-4}$ - $10^{-3}$  to 0.01-0.02, i. e., at  $\Theta$  values from 0.3-0.5 to 0.75-0.9. Thus it can be considered that a marked filling of the second and of subsequent layers begins when the filling of the first layer is 75-90% completed.

A comparison of the values of the specific surfaces as obtained by various methods is given in Table 1. The investigators who carried out the measurements on coked charcoal [7] determined its surface by the Langmuir equation since the BET method proved to be inapplicable. The value obtained by them was 1744 m<sup>2</sup>/g. More precise results are given by the method of [12] which is based on the complete BET equation and involves

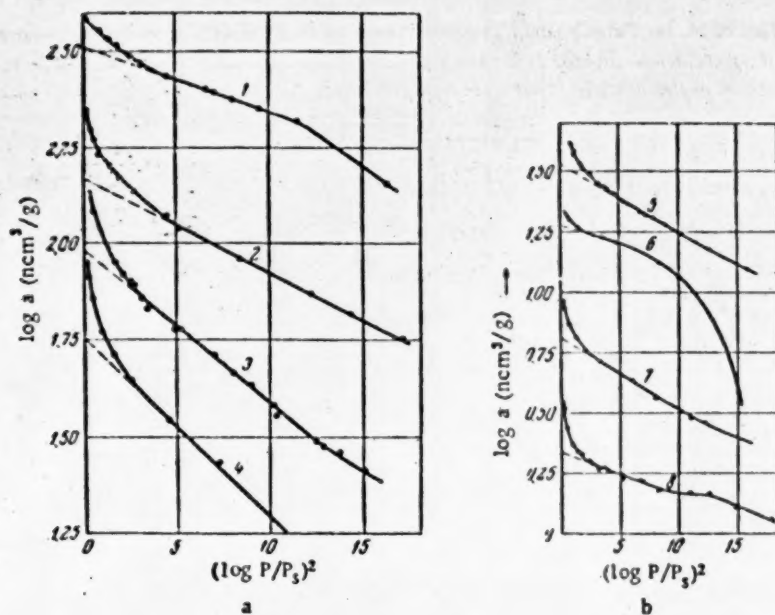


Fig. 2. Adsorption isotherms for nitrogen at 77-78° K in the coordinates of the equation of M. M. Dubinin and L. V. Radushkevich. The figures on these curves correspond to the numbers of the specimens in Table 1: a) specimens 1-4, b) specimens 5-8.

rather complicated calculations. The determination by this method gave the values  $n = 1.20$ ,  $C = 187$  and  $a_m = 356 \text{ ncm}^3/\text{g}$ , i. e.,  $S = 1550 \text{ m}^2/\text{g}$ . In the other cases, the values of  $S$  were calculated by the usual method and have been taken without change from the respective papers.

As is to be seen from Table 1, the divergence between the results which were obtained by the BET method and those resulting from the proposed procedure, amounts on the average to 4%, and reaches 9% for the coked charcoal which has very fine pores. The advantage of the proposed method is to be found in the fact that it makes possible a trustworthy determination of the surfaces of all adsorbents, even including the finely porous active charcoals. In addition, a method based on the measurement of adsorption at low pressures is convenient for the determination of the small values of the surfaces of nonporous substances. For fixing a surface it is sufficient to measure the adsorption at 2-3 points with  $p/p_s = 10^{-4}$ - $10^{-2}$  ( $p = 0.1$ - $10 \text{ mm Hg}$  for nitrogen at 77.4° K).

Equation (2) takes the following form:

$$\log \frac{a}{a_m} = -D \left( \log \frac{p}{p_s} \right)^2. \quad (3)$$

Representing the isotherms for various adsorbents in absolute units amounts to an equidistant displacement of these isotherms to the coincidence of point K with a point corresponding to the volume of the monomolecular layer adsorbed per unit of surface ( $10.2 \text{ } \mu\text{moles}/\text{m}^2$  for nitrogen at 77.4° K).

As is to be seen from Table 1 ( $D$  values) and from Fig. 2, the absolute adsorption isotherms for nitrogen on various adsorbents considerably differ from one another in the monomolecular region, a fact pointing to the perturbing action of the constriction of the pores. The coefficient  $D$ , which is approximated from the adsorption isotherms for nitrogen on powdered quartz and on coarsely porous silica gel [13], is equal to 0.04. This is in good agreement with the values for the coarsely porous adsorbents 3 and 4 in Table 1. Thus the absolute adsorption

isotherms for nitrogen on coarsely porous adsorbents at 77.4° K is characterized in the region under consideration by a D value equal to 0.040-0.045.

Thus the equation of M. M. Dubinin and L. V. Radushkevich describes with accuracy the monomolecular adsorption of nitrogen on various adsorbents at  $\theta$  values equal to 0.4-0.8 and by its use one is led to a new method for the determination of the specific surface areas of adsorbents.

#### LITERATURE CITED

- [1] A. G. Parts, *Austral. J. Appl. Sci.* 6, 183 (1955).
- [2] S. Chu Liang, *J. Appl. Phys.* 22, 148 (1951).
- [3] A. D. Crowell and D. M. Young, *Trans. Farad. Soc.* 49, 1080 (1953).
- [4] M. M. Dubinin and L. V. Radushkevich, *Proc. Acad. Sci. USSR* 55, 331 (1947).
- [5] M. M. Dubinin, E. D. Zaverina and L. V. Radushkevich, *J. Phys. Chem.* 21, 1351 (1947).
- [6] M. M. Dubinin and E. D. Zaverina, *J. Phys. Chem.* 23, 469 (1949).
- [7] J. de Dios Lopez-Gonzalez, F. G. Carpenter and V. R. Deitz, *J. Res. Nat. Bur. Stand.* 55, 11 (1955).
- [8] V. P. Dreving, A. V. Kiselev and O. A. Likhacheva, *J. Phys. Chem.* 25, 710 (1951).
- [9] V. P. Dreving, A. V. Kiselev and O. A. Likhacheva, *Proc. Acad. Sci. USSR* 82, 277 (1952).
- [10] L. G. Joyner and P. H. Emmett, *J. Am. Chem. Soc.* 70, 2353 (1948).
- [11] B. V. Ilyin, A. V. Kiselev et al., *Proc. Acad. Sci. USSR* 75, 827 (1950).
- [12] L. G. Joyner, E. B. Weinberger and C. W. Montgomery, *J. Am. Chem. Soc.* 67, 2182 (1945).
- [13] A. P. Karnaukhov, A. V. Kiselev and E. V. Khrapova, *Proc. Acad. Sci. USSR* 94, 915 (1954).

Received April 2, 1957

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## THE KINETICS OF THE DECOMPOSITION OF DIAZOMETHANE IN A STREAM OF NITROGEN

P. S. Shantarovich

(Presented by Academician V. N. Kondratyev, April 6, 1957)

The methylene radical,  $\text{CH}_2$ , takes part in a series of chemical reactions and the study of its interaction with the molecules of various substances ( $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CH}_4$  . . .) is therefore of particular interest for chemical kinetics. Since, however, methylene is itself a decomposition product it becomes necessary to study the kinetics of the breakdown of those substances which might serve as sources of  $\text{CH}_2$  radicals. Taking into account the fact that the life time of methylene varies, depending on the conditions of its preparation and the nature of the surrounding medium [1], we considered that it would be possible with the method of thermal decomposition of diazomethane in an inert gaseous medium to obtain  $\text{CH}_2$  in its normal condition and to study its reactivity.

Several papers are to be found in the literature in which there are presented the results of qualitative observations on the decomposition of diazomethane [2, 3]. Their authors have brought forward certain arguments in support of a monomolecular mechanism for the initial step:  $\text{CH}_2\text{N}_2 \rightarrow \text{CH}_2 + \text{N}_2$ . By the mirror method direct confirmation has been given of the formation of  $\text{CH}_2$  as the initial product of the breakdown of  $\text{CH}_2\text{N}_2$  [4].

### Methods and Results

Diazomethane, obtained by the decomposition of nitrosomethylurea in an alkaline medium, was dissolved in cold dibutylphthalate from which it was then carried into a receiver by a stream of pure nitrogen. Thus the concentration of  $\text{CH}_2\text{N}_2$  in the gas could be varied.

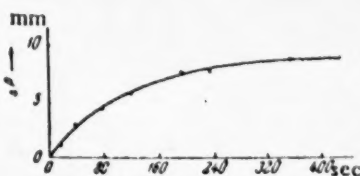
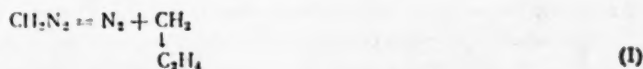


Fig. 1. The kinetics of the decomposition of  $\text{CH}_2\text{N}_2$  in  $\text{N}_2$  under stationary conditions.

In preliminary experiments it was established that only in an inert gaseous medium can the slow, continuous breakdown of diazomethane be observed at high temperatures. It was at the same time proven that at sufficiently high dilution, and with appropriate values of  $t$  and  $\sigma$ , ethylene is, aside from  $\text{N}_2$ , the sole product of the complete breakdown of diazomethane. The unreacted diazomethane can be separated out, either by low temperature distillation with subsequent complete decomposition in a stream of nitrogen or by adsorption by benzoic acid and analysis of the gaseous residue.

In Table 1 there are shown the results of observations on the decomposition of  $\text{CH}_2\text{N}_2$  in a stream of nitrogen. In Column 3 there is given the amount of  $\text{C}_2\text{H}_4$  which was separated out of the discharged reaction gases and in Column 5 the amount of ethylene which was obtained on decomposition the unreacted diazomethane. The sum of these quantities gives the content of  $\text{CH}_2\text{N}_2$  in the initial mixture and their ratio the extent of decomposition. In the last column of the table there are given values of the velocity constant, calculated for a reaction of first order. From all of this data it follows that the slow decomposition of diazomethane proceeds according to the equation:





Thus under stationary conditions, the relation:

$$2\Delta P = x \dots, \quad (1)$$

is valid for this reaction,  $x$  (mm) being the amount of decomposed  $\text{CH}_2\text{N}_2$ . In Fig. 1 there are presented the results of calculations on the kinetics of the decomposition of diazomethane, using a first-order reaction law and including the theoretical relation (1). The good agreement of the experimental points with the calculated curve confirms the mechanism of decomposition of diazomethane and the relationship between the resulting products. At higher concentrations of diazomethane in the gaseous mixture ( $\text{CH}_2\text{N}_2 + \text{N}_2$ ), the calculations agree with the experimental results only in the initial stage of the breakdown when there is an absence of complications from secondary reactions.

TABLE 1

The Breakdown of  $\text{CH}_2\text{N}_2$  in a Stream of  $\text{N}_2$ .  $P = 20$  mm,  $t = 381^\circ$

Liters of mixture taken	Time of contact, $\sigma$ , sec.	Found						Initial pressure of $\text{CH}_2\text{N}_2$ , $P_0$ , in mm	Decomposition in %	$P_0$ , mm	Decomposition constant $K$ , $\text{sec}^{-1}$
		unreacted $\text{CH}_2\text{N}_2$		reacted $\text{CH}_2\text{N}_2$		conc. $\text{CH}_2\text{N}_2$ in mixture, in %					
		$\text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{N}_2$		$\text{C}_2\text{H}_4 \rightarrow \text{CH}_2\text{N}_2$							
		$\text{cm}^3$	$\text{cm}^3$	$\text{cm}^3$	$\text{cm}^3$						
8.90	0.03	46.76	93.56	3.30	6.60	1.06	0.212	6.59	0.1981	2.27	
4.75	0.52	9.14	18.28	20.06	40.12	1.44	0.288	68.70	0.090	2.23	
4.15	0.49	3.39	6.78	7.90	15.80	0.52	0.104	72.30	0.029	2.62	
2.05	0.14	7.20	14.40	3.05	6.10	1.00	0.200	29.75	0.141	2.53	
3.55	0.08	17.58	35.16	3.72	7.44	1.20	0.240	17.46	0.198	2.40	
4.72	0.53	11.91	23.82	26.32	52.65	1.62	0.324	68.86	0.101	2.20	
4.50	0.50	4.83	9.66	12.50	25.00	0.77	0.154	72.14	0.043	2.55	
6.00	0.35	13.77	27.54	19.23	38.46	1.10	0.220	58.27	0.092	2.30	
4.40	0.50	6.40	12.80	15.60	31.20	1.00	0.200	70.90	0.057	2.50	

#### The Temperature Dependence of the Rate of Breakdown of Diazomethane

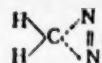
It can be supposed that in the breakdown of  $\text{CH}_2\text{N}_2$  secondary reactions take place between the  $\text{CH}_2$  and the initial diazomethane.



The results of kinetic investigations and, especially, very sensitive experiments with Te mirrors, show, however, that this reaction involves a high energy of activation or, in all likelihood, a high degree of steric hindrance. It follows from our experiments that a relatively small increase of the temperature of the decomposition of  $\text{CH}_2\text{N}_2$  (in the interval up to  $500^\circ$ ) sharply diminishes the time required for removal of a standard tellurium mirror, a fact which can only be explained by the low probability of Reaction (II) in the temperature range up to  $500^\circ$ . Thus the yield of ethylene is the result of the mere recombination of the methylene radicals, the initial products of the decomposition of diazomethane. From the  $\log K$  vs  $1/T$  relation we find the value  $E = 31,750$  cal. The complete expression for the rate constant for the thermal decomposition of  $\text{CH}_2\text{N}_2$  will have the form:

$$K = 0.8 \cdot 10^{11} e^{-\frac{31750}{RT}} \quad (2)$$

The value for  $E$  applies to the process of redistributing the bonds in the diazomethane molecule



this leading to the formation of two new particles:  $\text{CH}_2 + \text{N}_2$ . The magnitude of the coefficient of the exponential in the expression for  $K$  seems completely reasonable if comparison is made with the expression for the constant for the breakdown of nitrous oxide, a reaction in which the decomposition products are of similar nature.

## The Mechanism of the Decomposition of Diazomethane in a Stream of Nitrogen

Through the study of the temperature dependence of the rate of decomposition it has been established that the course of the logarithmic curve (Fig. 2) changes at  $t \geq 500^\circ$  with the result, as it proves, that the constitution of the decomposition products is also altered. Ethane, acetylene, and, in a small amount (1.0-1.5%), butane and propylene appear along with ethylene, the principle reaction product. The reaction tube becomes covered with a layer of carbon.

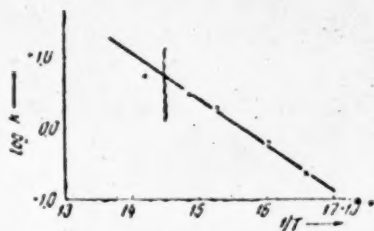


Fig. 2. The temperature dependence of the rate of decomposition of  $\text{CH}_2\text{N}_2$  in a stream of nitrogen.

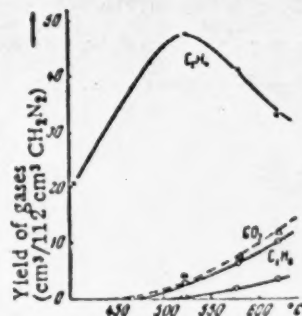
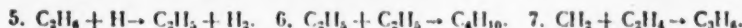
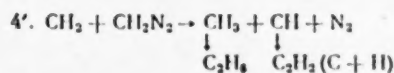
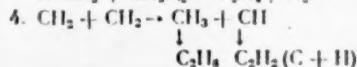
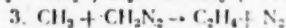


Fig. 3. The temperature dependence of the yield of the decomposition products from  $\text{CH}_2\text{N}_2$ .  $\text{C}_{\text{CH}_2\text{N}_2} = 2.62\%$ .

The alteration of the hydrocarbon make-up which results from varying the temperature of the  $\text{CH}_2\text{N}_2$  decomposition is shown in Fig. 3. The dotted curve indicates the amount of  $\text{CO}_2$  which was obtained by burning the carbon deposited on the walls of the reaction tube. These results, which have been obtained by mass spectroscopic and by chemical analyses, give adequate grounds for considering that under the conditions of our experiments the mechanism of the thermal decomposition of diazomethane is covered by the following series of reactions:



It is clear that the first two of these reactions are basic processes for the decomposition of diazomethane which can be realized under all conditions. At  $t < 450^\circ$  and in an inert gaseous medium this reaction path is clearly the only one which can be considered as completely established. At  $t \geq 500^\circ$  secondary reactions of the methylene radical become possible. Of these, reactions 5, 6, and 7 are of small significance. The maximum total yield of the higher hydrocarbons ( $\text{C}_3 + \text{C}_4$ ) exceeds 1.5%.

The mechanism of the formation of ethane possesses special interest. It is clear, however, that its appearance in the decomposition products can be explained in only two ways: either by reactions of disproportioning the methylene radicals (4) or by interaction of the latter with the original molecules of diazomethane (4'). It is impossible to give a convincing argument looking either to an exclusive selection of one of these possible reactions or to fixing the share of each in a combined action. Completely analogous conditions are also to be found in the reaction of the decomposition of ketene. Thus from the temperature dependence of the yield of

ethane (at  $t > 500^\circ$ ) in the decomposition of diazomethane or of ketene, it is not possible to establish the magnitude of the activation energy for the reaction of disproportionating the methylene radicals. From the course of the curves showing the formation of  $C_2H_4$  and  $C_2H_2$  (Fig. 3) it is only possible to suppose that this quantity must be of the order of 18-20 kcal.

#### LITERATURE CITED

- [1] G. Pearson, R. Parcell and G. Saigh, *J. Am. Chem. Soc.* 1938, 409.
- [2] E. W. R. Steacie, *J. Phys. Chem.* 35, 1493 (1931).
- [3] R. G. W. Norrich and F. W. Kirkbride, *J. Chem. Soc.* 1933, 119.
- [4] F. Rice and A. Glasebrook, *J. Am. Chem. Soc.* 56, 2381 (1934).

Received April 2, 1957

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# A POLAROGRAPHIC INVESTIGATION WITH A BACKGROUND OF MOLTEN BORAX.

## THE POLAROGRAPHY OF COPPER AND CADMIUM

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The polarography of molten salts has recently attracted more and more attention [1, 2]. The direct polarographic analysis of melts (metallurgical slags and industrial molten electrolytes) has considerable practical interest. In this respect, however, the oxides have been less thoroughly investigated. In the present communication there are presented the results of a polarographic study of oxides of copper and cadmium dissolved in molten borax.

This study was carried out on an automatic recording polarograph, to which there was connected a M 21-2 mirror galvanometer with a sensitivity of  $1.5 \cdot 10^{-9}$  amp/mm. An unglazed porcelain crucible served as the electrolysis cell. The cathode was a platinum wire, 0.25 mm in diameter, and the anode a plate of 2.5 cm<sup>2</sup> area. Renewal of these electrodes by depolarization was brought about by short circuiting them. The experiments were carried out at 820°. In Fig. 1 there are shown polarograms of CuO and CdO at identical concentrations and also a polarogram of the background, which decomposes at a potential of 1.34 v. For both of these oxides we have established a direct proportionality between the strength of the diffusion current and the mole fraction of the dissolved oxide

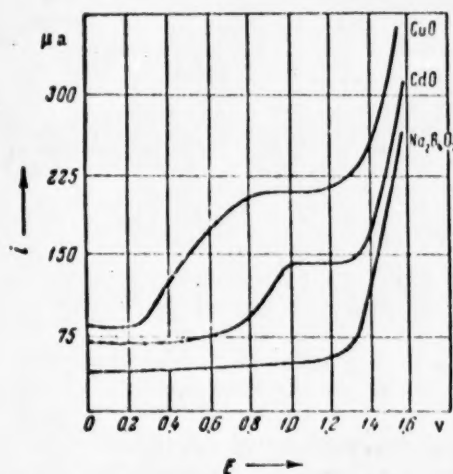


Fig. 1. The polarograms of the oxides of copper ( $N_{CuO} = 0.009675$ ) and cadmium ( $N_{CdO} = 0.0060$ ), and borax (background).  $t = 820^\circ$ ;  $\delta = 1/2500$ .

$$i_d = kN. \quad (1)$$

Black and DeVries [3] have found that the polarogram for a  $KCl-ZnCl-NiCl_2$  melt, obtained with platinum electrodes and at a temperature of 413°, is satisfactorily described by the equation of Kolthoff and Lingane [4]

$$E = E_M - \frac{2.3 RT}{nF} \log \frac{k_s}{j_0} + \frac{2.3 RT}{nF} \log (i_d - i). \quad (2)$$

In certain earlier investigations [5-7] it has been shown that the polarographic waves obtained with platinum electrodes in molten salts are described, not by Eq. (2), but by the Geitrovsky-Ilkovich equation:

$$E = E_{\frac{1}{2}} - \frac{2.3 RT}{nF} \log \frac{i}{i_d - i}. \quad (3)$$

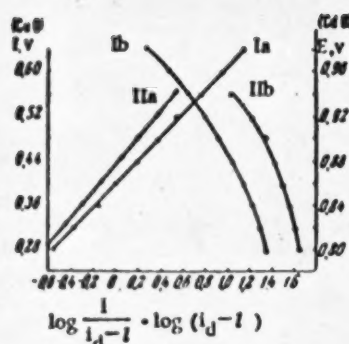


Fig. 2. The dependence of  $\log \frac{1}{i_d - i}$  (curves a) and  $\log (i_d - i)$  (curves b) on the applied potential: I) for copper oxide ( $N_{\text{CuO}} = 0.00194$ ), II) for cadmium oxide ( $N_{\text{CdO}} = 0.0060$ ).

values of the half-wave potentials were found and were then compared with the corresponding concentrations. The results obtained are given in Table 1. Here there are also included values of  $i_d/N$ , as well as calculated and experimentally determined values of the coefficient of the logarithmic term in Eq. (3). As is to be seen from this data, the quantity  $i_d/N$  is nicely constant at a fixed value of the sensitivity, this confirming the validity of Eq. (1) and pointing up the precision of those determinations of the concentrations of oxides in melts which make use of measurements of diffusion currents. Since the dependence of  $E_{1/2}$  on  $\log N/2$  is not linear, the application of Eq. (4) to the melts investigated by us is not justified. There are good grounds for speaking here of the constancy of the half-wave potentials, a fact which is in good agreement with Eq. (3).

At 820° the coefficient  $2.3 RT/nF$  of the logarithmic term must have the following theoretical values: 0.226 for  $n = 1$ , 0.113 for  $n = 2$ , and 0.075 for  $n = 3$ . For copper oxide the experimentally determined coefficient most closely corresponds to either  $n = 2$  or  $n = 1$ , a fact which can possibly be explained by the occurrence of

TABLE 1

Oxide	Mole fraction, N	$E_{1/2}$	$\frac{i_d}{N} \cdot 10^{-5}$	$\frac{\Delta F}{2.303 RT} \log \frac{1}{i_d - i}$	Sensitivity
CuO	0.000485	0.300	15.4	0.103	1/1000
	0.000970	0.432	15.5	0.210	
	0.001455	0.378	15.5	0.155	
	0.001940	0.400	15.7	0.209	
	0.003870	0.420	12.6	0.209	
	0.005805	0.378	12.6	0.168	1/2500
	0.007740	0.418	12.6	0.185	
	0.009675	0.456	12.7	0.232	
CdO	0.0005	0.884	13.5	0.070	1/1000
	0.0010	0.898	13.5	0.070	
	0.0015	0.894	13.0	0.138	
	0.0020	0.870	12.8	0.081	
	0.0020	0.896	9.4	0.118	
	0.0040	0.896	9.4	0.094	1/2500
	0.0060	0.874	9.4	0.103	
	0.0080	0.904	9.4	0.063	
	0.0100	0.885	9.4	0.093	
	0.0120	0.854	9.4	0.098	

In order to clear up the question as to which equation would describe polarographic waves on solid electrodes in the melts investigated by us, graphs were constructed in the coordinate  $E, \log (i_d - i)$  and  $E, \log \frac{1}{(i_d - i)}$ .

The points in question were taken from our experimental data. Examples of such graphs are shown in Fig. 2. From these it follows that the polarographic waves are described by Eq. (3) and not by Eq. (2). From the equation of Koltzoff and Lingane it follows that the half-wave potentials should depend on the concentration, i. e.,

$$E_{1/2} = E_M^0 + \frac{2.3 RT}{nF} \log K' f_s + \frac{2.3 RT}{nF} \log \frac{N}{2}, \quad (4)$$

$N$  being the mole fraction of the dissolved material.

Using the graphs constructed from our experimental data,

TABLE 2

$N_{\text{CdO}} = 0.008$			$N_{\text{CdO}} = 0.006$		
$T, ^\circ K$	$i_d, \mu A$	$\log i_d$	$T, ^\circ K$	$i_d, \mu A$	$\log i_d$
1040	21.6	1.334	1048	15.0	1.176
1061	33.6	1.526	1078	26.2	1.418
1083	41.3	1.616	1093	31.7	1.501
1109	65.3	1.815	1113	41.2	1.615
1133	75.0	1.875	1133	47.2	1.674
			1148	60.0	1.778

thermal dissociation,  $2\text{CuO} \rightleftharpoons \text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2$ , at high temperatures. Even at 1008° the pressure of oxygen above cupric oxide reaches the value of the partial pressure of oxygen in the atmosphere [8].

For cadmium oxide the coefficient of the logarithmic term,

$$\frac{2.3 RT}{nF}$$



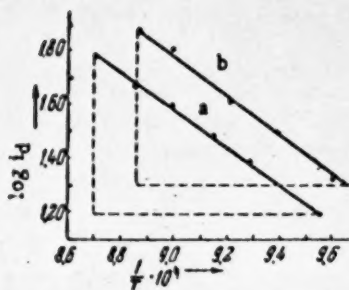


Fig. 3. The temperature dependence of the diffusion current in melts containing cadmium oxide. a)  $N_{\text{CdO}} = 0.006$ ; b)  $N_{\text{CdO}} = 0.008$ .

corresponds to either  $n = 2$  or  $n = 3$ . This latter value is understandable if complex ions are assumed to exist in the melt.

For melts containing CdO, the temperature dependence of the diffusion current was developed over the interval from 760 to 875°. The results of these experiments are given in Table 2.

It is to be seen from Fig. 3 that graphs constructed in the coordinates  $\log i_d, 1/T$  are almost linear, this indicating the validity of the equations:

$$\ln i_d = A - \frac{B}{T} \quad (5)$$

$$i_d = k e^{-\frac{U}{RT}} \quad (6)$$

with  $A = \ln k$  and  $B = U/R$ .

From the value of the slope of the straight line representing Eq. (5) it is possible to calculate the energy of activation, which, for our case, proved to be equal to 31.27 kcal/mole.

#### LITERATURE CITED

- [1] Yu. S. Lyalikov, *J. Anal. Chem.* 8, 38 (1953).\*
- [2] N. G. Chovnyk, *J. Phys. Chem.* 30, 277 (1956).
- [3] E. Black and Th. DeVries, *Anal. Chem.* 27, 906 (1955).
- [4] I. Kolthof and D. Lingane, *Polarography* [in Russian] (Moscow, 1948), p. 161.
- [5] Yu. K. Delimarsky and I. D. Panchenko, *Ukr. Chem. J.* 19, 47 (1953).
- [6] Yu. K. Delimarsky and I. D. Panchenko, *Proc. Acad. Sci. USSR* 91, 115 (1953).
- [7] I. D. Panchenko, *Ukr. Chem. J.* 22, 153 (1956).
- [8] W. D. Treadwell, *Zs. Elektrochem.* 22, 414 (1916).

Received March 5, 1957

\* Original pagination. See C. B. translation.

## A DIELECTRIC INVESTIGATION OF THE PHASE TRANSFORMATIONS IN THE SYSTEM SOAP - HYDROCARBON - WATER

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The phase structures of soaps determine in many respects the action of the latter as thickeners in lubricating greases. The solvents and the hydroxyl-containing compounds which are added to them have a considerable effect on the temperatures of phase transitions in soaps [1]. The determination of the relationship which exists between the phase transformations in a soap and in a system which has been thickened with this soap possesses much interest. For this purpose various methods - thermal, x-ray and optical analyses, etc. - are used, since it is necessary to apply several independent techniques in order to disclose the various phase transformations.

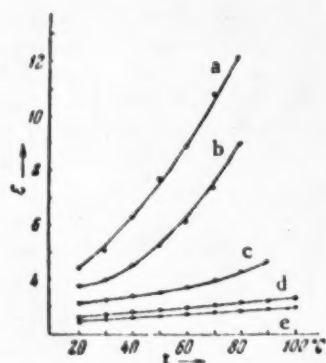


Fig. 1. The temperature dependence of the dielectric constant in the system calcium oleate-xylene: a) 1 kilocycle per second, b) 10 kilocycles per second, c) 50 kilocycles per second, d) 450 kilocycles, e) 1.5 megacycles per second. Concentration, 80 g per 100 ml of solvent.

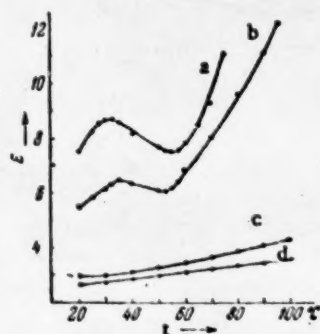


Fig. 2. The temperature dependence of the dielectric constant in the system calcium oleate-xylene-water (polyhydrate): a) 1 kilocycle per second, b) 10 kilocycles per second, c) 450 kilocycles per second, d) 1.5 megacycles per second. Concentration, 80 g per 100 ml of solvent.

In studying the phase transformations in a soap-hydrocarbon system, we have resorted to measurements of the dielectric constant, the dielectric properties of many substances being substantially altered as a result of structural transformations [2].

In an investigation of the temperature dependence of the dielectric constant, Doscher and Davis [3] showed the existence of phase changes in the system sodium stearate-cetane-water.

As the subject of study we have selected the xylene-calcium oleate system, this being characterized by phase transitions at low temperatures. According to the data of Trapeznikov and Zakieva [4] phase changes exist at 50-55° and 75-80° in the calcium oleate-water system, and at 50° and 71.5° in the calcium oleate-water-velosite system.

Capacity measurements over the interval from 1 to 10 kilocycles per second were carried out on an audio-bridge and, over the interval from 50 kilocycles to 1.5 megacycles per second, on a Q-meter. In order to allow for the capacity of the supply leads in the calculation of the dielectric constant, measurements were made with a standard liquid (m-xylene). The error in the dielectric constant determinations varied with the method employed, the frequency and the magnitude of the constant itself. On the average this error amounted to 1-5%.

Figure 1 presents the results of measurements of the temperature dependence of the dielectric constant in a system containing 80 g of calcium oleate dissolved in 100 ml of xylene. The effect of additions of water is shown in Figs. 2 and 3. In all of the investigated systems the dielectric constant diminishes with an increase of frequency. This effect is especially pronounced in those systems which contain water. As the frequency increases the  $\epsilon$  vs  $t$  curves level off. The marked dependence of the dielectric constant on the frequency points to a low frequency Maxwell-Wagner polarization such as exists in the presence of two phases differing in dielectric constant and in conductivity [5].

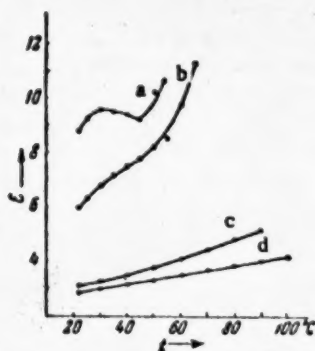


Fig. 3. The temperature dependence of the dielectric constant in the system calcium oleate-xylene-water (monohydrate): a) 1 kilocycle per second, b) 10 kilocycles per second, c) 450 kilocycles per second, d) 1.5 megacycles per second. Concentration, 30 g per 100 ml of solvent.

groups of the soap molecules which results from phase transformations [3]. The displacement of the minimum in the dielectric constant which is observed in a system containing 1 mole of water per 1 mole of soap gives indication of a lowered transition temperature for the monohydrate of calcium oleate in the hydrocarbon. Thus the addition of water to the soap leads to a decrease of the phase transition temperatures. Free water, which does not interact with the soap, is without influence on these temperatures.

The higher values of the dielectric constant in systems containing water, as compared with the water-free systems, is the result, first, of the hydration of the soap molecules, which increases their polarity and, second, of the peptizing action of water. The special role of water in the structure of soap-hydrocarbon systems was also noted in studies on their mechanical, thermal and optical properties [6].

It has been established that the heating and cooling curves of this system differ considerably from one another because of supercooling. The dielectric constant proved to be sensitive also to recrystallization in the system, a process which continues over several days.

Thus a study of the dielectric constant can give valuable information concerning the phase transformations in a soap-hydrocarbon-water system.

#### LITERATURE CITED

- [1] G. V. Vinogradov, Symposium, Lubricating Greases [in Russian], 1951, p. 12.
- [2] C. P. Smyth, Dielectric Behavior and Structure, Ch. V (N. Y., 1955), p. 132.

- [3] T. M. Doscher and S. Davis, *J. Phys and Coll. Chem.*, 55, 1, 53 (1951).
- [4] A. A. Trapeznikov and S. Kh. Zakieva, *Trans. All-Union Conference on Colloidal Chemistry* (Kiev, 1952), p. 362. \*
- [5] A. Gemant, *The Electrophysics of Insulating Materials* [in Russian] (Leningrad, 1932), p. 100.
- [6] A. A. Trapeznikov, *Symposium, The Low Temperature Properties of Petroleum Products* [in Russian] (Moscow, 1949), p. 98.

Received April 8, 1957

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\* In Russian.

## THE INFLUENCE OF GASES ON THE FLOATABILITY OF CERTAIN NONSULFIDE MINERALS AND ITS DEPENDENCE ON THEIR CRYSTAL STRUCTURES

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E. M. Chaplygina

A study of the influence of gases on the flotation of nonsulfide minerals has made it possible to establish those various adsorptive and flotational properties of fluorite and barite which result from their interaction with gases [1].

Thus even in the absence of a collector, fluorite will float in pulps with a high concentration of dissolved oxygen whereas barite will enter into the froth, even at the highest oxygen saturation in the pulp, only if a collector is present.

It has been noted that an extended treatment with nitrogen is without essential influence on barite which has earlier been subjected to the action of oxygen, the barite stubbornly retaining its previously acquired ability to float. In distinction from barite, the floatability of fluorite is diminished by an insufficiency of oxygen in the pulp and the flotation effect which is achieved is the greater, the higher the concentration of oxygen in the solution. After a careful treatment with nitrogen, fluorite loses its ability to float and the collector adheres to the mineral.

Investigations which were carried out on pure minerals—fluorite from the Transbaikal region and barite from the Turkmen SSR—using the precision apparatus described earlier in [10] have confirmed the facts outlined above. These experiments were performed with minerals having grain sizes of 0.1–0.074 mm; the mineral batch amounted to 20 g, the dosage of sodium oleate was 50 g/ton and the flotation was carried out without addition of alkali, sol.:liq. being equal to 1:5.

The preparation of the minerals for the experiment, the removal of oxygen from the water and the flotation were all carried out in a current of argon (purity, 99.95%) and nitrogen (purity 99.50%) the latter having been freed from the contaminating oxygen in an electric furnace which was filled with granulated copper oxide. Active copper was obtained by reduction with hydrogen during heating of this furnace to 450° [2]. Analysis for the insignificantly small amounts of oxygen in the purified gas was by the colorimetric method of Mugdan [3]. The nitrogen employed in these experiments was free of oxygen.

Experiment showed that 44% of the fluorite went over into the concentrate as a result of flotation in a pulp with a normal concentration (9.55 mg/liter) of dissolved oxygen. After carefully removing the adsorbed oxygen from the surface of the mineral and decreasing the oxygen concentration in the pulp to 0.20 mg/liter, the floatability of the fluorite sharply diminished, the yield of mineral in the froth amounting to only 4–5%. As the concentration of the oxygen in the pulp was raised to 7 mg/liter, then to 33.88 mg/liter and finally to 41.35 mg/liter, the yield of fluorite in the concentrate also increased, rising to the respective values, 15.15, 53.20 and 81.20%. At high concentrations of oxygen in the pulp the time of flotation was cut by a factor of 2, going from 15–20 to 6–10 minutes.

Under similar conditions, flotation experiments in nitrogen and argon showed no pronounced decrease in the floatability of a barite, the surface of which had been earlier altered by treatment with oxygen. In flotation of pulps at the lowest oxygen concentrations (0.17–0.20 mg/liter), the extraction of barite in the concentrate remained fixed at 95.8–97%.



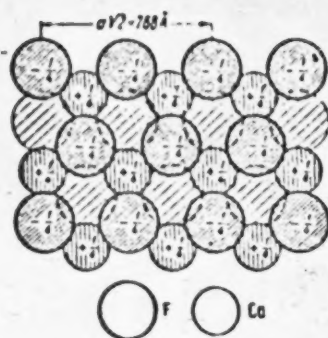


Fig. 1. A projection of the structure of fluorite,  $\text{CaF}_2$ , on the cleavage plane (111).

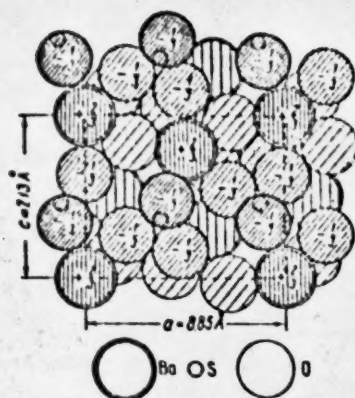


Fig. 2. A projection of the structure of barite,  $\text{BaSO}_4$ , on the cleavage plane (010).

All of this indicates that the flotational activity of barite is changed only slightly by an alteration of the concentration of oxygen in solution provided that oxygen has earlier been adsorbed on the barite surface. On the other hand, the flotation of fluorite depends to a marked degree on the oxygen content of the pulp; the introduction of oxygen into solution makes possible a better flotation of the fluorite, increasing the rate of adhesion of the particles to the air bubbles and diminishing the flotation time. The collecting action of sodium oleate increases with an increase of the oxygen concentration in the one phase.

The above established relation between the flotational behavior of fluorite and barite can possibly be explained in terms of peculiarities in crystal structures, account being taken of the fact that the disintegration which occurs in minerals during a grinding process is for the most part along cleavage planes, i. e., along planes which have definite crystallographic and crystallochemical properties, and that the molecular-physical properties of the surfaces thus formed are determined by their chemistry and topography.

In Figs. 1 and 2 there are shown projections of the fluorite and barite structures on their cleavage planes\* [4-6]. The diminution in the intensity of coloring indicates the degree of recession of the ions below the surface. In these figures values are given for the uncompensated electrostatic charges; for barite the calculation of these latter has been carried out very approximately, no account being taken of the degree of covalency of the bonds [7].

In fluorite there is observed a uniform distribution of positive and negative charges of equal magnitudes. The difference in the spacing of their centers is not great (0.785 Å with the ionic radii, calcium 1.04 Å and fluorine 1.43 Å). The hollows above the fluoride ions of the lower layer are relatively small and they are screened by the ions of the overlying layers. Thus the fluorite surface is distinguished by a low relief and the molecular field of its surface is characterized by its uniformity and by the small value of its intensity, the individual uncompensated electrostatic charges being no greater than  $\frac{1}{4}$ .

On the other hand, the surface of barite is characterized by a pronounced difference in the values of the uncompensated charges and by a sharply expressed nonuniformity in the distribution of these charges in the faces of the elementary cell. Along with a certain "openness" in the ionic distribution and a marked unevenness in the distribution (the difference in the spacing of the charge centers in the surface layers amounts to 2 Å with the ionic radii, 1.38 Å for barium and 1.36 Å for oxygen) there results a nonuniformity in the molecular field of the surface and an increased intensity of this field in the positions of localization of the active centers, the charges with values  $> \frac{1}{2}$ .

From what has been said there follows first of all an explanation of the difference in the ability of these two minerals to undergo hydration. Thus the lowered hydrateability of the fluorite surface as compared with

\* Incomplete cleavage along the (010) plane is used here as most graphically reflecting the character of the energetic and topographic differences in the surface layers of the two minerals.

the barite which makes it possible to speak in certain cases of the natural floatability of the former results, first, from a smaller value for the uncompensated charges and, second, from a more unfavorable ratio between the areas of the adsorbed water molecule and the "elementary cell" of  $\text{CaF}_2$  [8]. This last implies that the cross-sectioned area of the molecule is large in comparison with the field of action of the corresponding ion and that a part of the molecules cannot move up to direct contact with the attracting ions. In addition, the relative uniformity of the surface and the absence of strong charges favor instability and mobility in the hydrate layer.

In a similar fashion, the peculiarities of the molecular field of the surface determine the behavior of gases dissolved in the pulp, the interaction of these gases with the mineral surface leading to physical adsorption if chemical effects are left out of account. As a result of the screening of the strong field of the surface by the adsorbed molecules there is a change in the surface's ability to hydrate. On the regularity of the dipoles in this hydrate film there depends in turn that diffusion of gas to the surface, which must precede adsorption. Clearly there is a direct relationship between the degree of hydration of a surface and the adsorption of gases by it.

The increase of the hydrophobic character of a surface which results from the physical adsorption of gases from solution should in general be related to the value of the intensity of the surface field. This is a reciprocal relation: the smaller the field intensity, the greater the effect of screening it by adsorbed molecules. For example, oxygen without a collector exerts no effect on the flotation of barite or quartz [1] ("strong" fields) but considerably improves the flotation of fluorite (a "weak" field) even to the extent of making it possible to float the latter in highly saturated pulps without a collector.

The irreversibility of the effect of oxygen on the flotation of barite is in all likelihood connected with the especial stability of the binding of a part of the oxygen molecules at definite centers on the barite surface, the inhomogeneous nature of this surface fully justifying such a conception. Here there is met a case in which there must be taken into account not only the physical character of the adsorption but also the possibility of a superimposed chemical effect. This question demands special consideration and in the present work we limit ourselves simply to this remark.

In the case of oxygen, a strongly electronegative element possessing an affinity for electrons, a superimposed chemisorption is undoubtedly present in view of the fact that a majority of the crystals contain some sort of microdefects [9] which lead to nonuniformity in the surface energy states and serve as adsorption centers. Obviously the chemisorbed ions or molecules of oxygen can in their turn activate the surface of the adsorbent, or at least a definite portion of it, permitting the subsequent adsorption of the molecules of the collector. It is exactly this side of the specific action of oxygen which leads in the general case to an enhanced action in adsorption and flotation as compared with other gases.

#### LITERATURE CITED

- [1] I. N. Plaksin and E. M. Chaplygina, *Bull. Acad. Sci. USSR, Div. Tech. Sci.* No. 9 (1952).
- [2] V. G. Fastovsky, *Oxygen* No. 2 (1951).
- [3] Mugdan, *Angew. Chem.* 5 (1933).
- [4] J. D. Dana et al., *System of Mineralogy* [in Russian] (Foreign Lit. Press, 1953).
- [5] N. V. Belov, *Mineral Symposium, Lvov Geol. Soc.* No. 4, 25 (1950).
- [6] P. Hartman and W. Perdok, *Acta Cryst.* 8, 9, 521 (1955).
- [7] L. Pauling, *The Nature of the Chemical Bond* [in Russian], 1947.
- [8] B. V. Ilyin, *The Nature of Adsorptive Forces* [in Russian], 1952.
- [9] A. Riz, *The Chemistry of Crystals with Defects* [in Russian] (Foreign Lit. Press, 1956).
- [10] I. N. Plaksin and S. V. Bessonov, *Bull. Acad. Sci. USSR, Div. Tech. Sci.* No. 1 (1954).

Received May 20, 1957

## THE MECHANISM OF FUSION OF ORGANIC GLASSES

N. A. Grishin, S. S. Voyutsky and M. M. Gudimov

(Presented by Academician V. A. Kargin, April 18, 1957)

The nature of the phenomena which lie at the basis of the important practical process of fusing organic glasses has until recently remained unclear. Starting from the widely held opinion that adhesional phenomena result solely from the action of molecular forces [1, 2], the attempt can be made to reduce the fusion of organic glasses to a softening of the abutting surfaces of the high polymers with a resulting increase of the true surface of contact. As was shown in [3, 4], however, the action of the molecular forces is in itself completely insufficient to assure more or less considerable forces of adhesion between two high-molecular specimens, even if these specimens are brought into the very closest contact.

It is also impossible to draw on the electrical theory of adhesion, as proposed by Deryagin and Krotova [3, 5], for the explanation of the mechanism of glass fusion since autoadhesion (autoadherence) is involved here and the formation of an electrical double layer is unlikely.

The phenomenon of fusion of organic glasses can be most simply explained on the basis of the diffusional mechanism of autoadhesion [6-10].

In the present communication certain experimental data are presented to support the claim that the fusion of glasses involves the diffusion of molecular chains, or even segments, of the one specimen into the other. This work was carried out on the plasticized and the unplasticized forms of an industrial organic glass - polymethylmethacrylate - which contained 6% dibutylphthalate.

Two rectangular plates of the organic glass with plane milled edges were inserted between two slabs of a thermal insulating material; the ends which were to be fused together were pressed one onto the other by a force directed along the plane of the plates and the region of contact was heated with narrow electrical resistance heaters which were inserted in the slabs. The fusion apparatus permitted the force of compression to be varied over a rather wide interval. The presence of the slabs in the apparatus precluded any appreciable deformation of the specimens, which as a result of heating are softened at the point of contact. After reaching the desired temperature, which required 15-20 minutes, the specimens were held in position for a definite period of time (the time of fusion) and were then cooled without being taken from the apparatus.

In certain cases the fused specimens thus obtained were subjected to a supplementary thermal treatment. In practice thermal treatment of fused specimens is resorted to in order to eliminate residual strains in an organic glass and to diminish the deformation in the region of the weld.

The tensile strength perpendicular to the plane of contact was measured in the fused specimens, use being made of a dynamometer of the type usually employed for such purposes. As a rule, rupture in the fused specimens occurred along the surface of initial contact.

It is significant that during loading of the specimens up to rupture no lack of uniformity in the strain distribution could be observed with polarized light in the plane of the fused seam. On this ground it can be considered that the values obtained for the rupture resistance are quantitatively characteristic of the autoadhesional strength. It should, however, be noted that the autoadhesional strength  $\sigma$ , evaluated in this way, is not completely determined by the diffusion of the macromolecules, or of their segments, at the time of welding. Naturally, diffusion

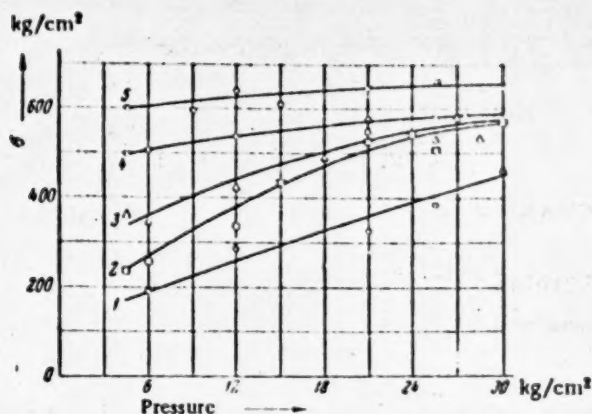


Fig. 1. The relation between the autoadhesional strength of specimens of plasticized polymethylmethacrylate and the pressure during fusion: 1) fusion temperature, 125°; 2) 135°; 3) 150°; 4) 160°; 5) 190°.

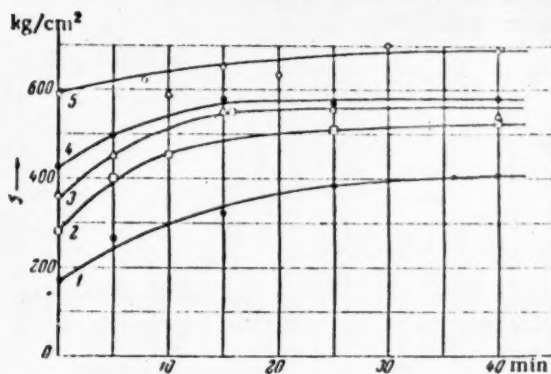


Fig. 2. The relation of the autoadhesional strength of specimens of plasticized polymethylmethacrylate to the duration of fusion: 1) fusion temperature 125°; 2) 135°; 3) 150°; 4) 160°; 5) 190°.

is continuing, both at the end of the heating period of the specimen and at the beginning of the cooling period, but since the conditions of heating and cooling were always the same, diffusion in these periods could not essentially affect the regularities which have been established by us.

In Fig. 1 there is shown the relation between the autoadhesional strength of specimens of plasticized polymethylmethacrylate and the pressure, at various fusion temperatures. The duration of fusion amounted to 15 minutes. In their general character the curves of Fig. 1 resemble similar curves for polyisobutylene [7]. The autoadhesional strength increases with an increase of pressure and tends toward a definite limit. The higher the temperature the less does the strength increase with rising pressure. This is to be explained by the fact that with the softening of the material there is a decrease in the pressure which is needed for realizing full contact of the fused surfaces. The fact that the maximum adhesional strength of polymethylmethacrylate lies at considerably higher pressures than is the case with polyisobutylene indicates that it is much more difficult to bring about complete surface contact in the fusion of rigid glasses.



With a relatively short fusion time (15 minutes), the maximum value of the adhesional strength was reached at most of the experimental temperatures under a pressure of  $20 \text{ kg/cm}^2$  and we therefore carried out all further fusion experiments at this same pressure.

In Fig. 2 there is shown the dependence of the autoadhesional strength of specimens of plasticized polymethylmethacrylate on the duration of fusion at various temperatures.

The curves which are presented in Fig. 2 are similar in form to the analogous curves for polyisobutylene [7, 8]. That these curves do not begin at the origin for zero time of fusion is of course to be explained by the fact that diffusion can take place to a certain degree even in the process of elevating the temperature to the fusion point.

At fusion temperatures of  $135\text{--}190^\circ$  the maximum autoadhesional strength is established in a relatively short period of time, 10-15 minutes. It is interesting that the limit of autoadhesional strength at the  $190^\circ$  temperature corresponds approximately to the cohesional strength of the material ( $700 \text{ kg/cm}^2$ ).

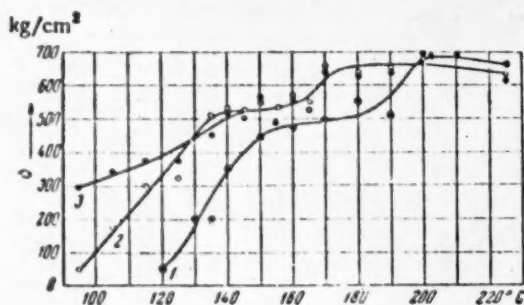


Fig. 3. The relationship between the autoadhesional strength and the temperature of fusion for: 1) unplasticized polymethylmethacrylate, 2) plasticized polymethylmethacrylate, 3) the same, but the fused samples were subjected to an additional thermal treatment.

The data which has been experimentally obtained on the relationship between the autoadhesional strengths of plasticized and unplasticized polymethylmethacrylate and fusion temperature is presented in Fig. 3. In these experiments the duration of fusion amounted to 15 minutes. After fusion, a part of the specimens of plasticized polymethylmethacrylate were subjected to thermal working for 60 minutes at  $135^\circ$ .

As can be seen, in the case of plasticized polymethylmethacrylate the autoadhesional strength reaches its limit at  $150^\circ$ . This limit is approximately equal to  $500 \text{ kg/cm}^2$  and does not change with the fusion temperature over the  $150\text{--}180^\circ$  range. However, at temperatures somewhat above  $180^\circ$  the curve once more sharply rises and the autoadhesional strength reaches  $700 \text{ kg/cm}^2$ , a value which corresponds to the cohesional strength of the material in the weld zone. The significant decrease in the strength at temperatures above  $210^\circ$  is in all likelihood the result of the thermal destruction of the material.

The two-stage character of the curve of autoadhesional strength vs temperature can be explained by the fact that over the  $150\text{--}180^\circ$  temperature interval the polymethylmethacrylate is in the high elastic condition, this state there can diffuse only separate portions of the molecular chains but not entire molecules, this resulting in a lower value for the autoadhesional strength than for the cohesional strength. The course of the curve in the temperature interval from  $150\text{--}180^\circ$  is almost a parallel to the axis of abscissas and points to an invariant mechanism of autoadhesion in the region of the high elastic state.

At temperatures above  $180^\circ$  the high polymer goes over into the condition of a viscous fluid in which displacement of the separate macromolecules with respect to one another becomes possible. Under these conditions the diffusion of molecules as a whole leads to the complete regeneration of the high-polymer structure in the zone of contact. As a result the material becomes monolithic and rupture experiments give values which are equal to the cohesional strength. The exhaustion of the heterogeneous material in the region of the weld is indicated by the fact that here rupture of the specimen frequently occurs at a position other than that of the weld.

However, it is possible that the high temperature regeneration of the polymer structure in the weld zone is also aided by the disintegration and recombination of the high polymer molecules which takes place under these conditions. The great significance of such phenomena in the flow of cellular high polymers under the action of large forces has been recently pointed out by Sogolova and Kargin [11].

The curve for plasticized polymethylmethacrylate has the same character, but is displaced to the left, the plasticizer lowering the temperatures for transition of the high polymer into both the high elastic and the viscous fluid condition.



With fusing temperatures above 135° the curve for specimens of a plasticized high polymer which have been subjected to subsequent thermal treatment merges with the curves for these same specimens when unworked. At lower fusion temperatures the adhesional strength is considerably higher in the case of thermal treatment. This is also completely understandable: with fusion temperatures below 135°, a comparatively long thermal treatment at 135° results in the deeper penetration into the one polymethylmethacrylate specimen of separate portions of the macromolecules of the other specimen thus aiding in the increase of the autoadhesional strength. At weld temperatures above 135°, thermal treatment at 135° is ineffective.

#### LITERATURE CITED

- [1] A. D. McLaren and C. H. Hofrichter, Paper Trade J. 125, 96 (1947).
- [2] A. D. McLaren, J. Polymer Sci. 3, 652 (1948).
- [3] B. V. Deryagin, Bull. Acad. Sci. USSR No. 7, 10 (1954).
- [4] S. S. Voyutsky, A. I. Shapovalova and A. P. Pisarenko, Proc. Acad. Sci. USSR 105, 1000 (1955).
- [5] B. V. Deryagin and N. A. Krotova, Adhesion [in Russian] (Acad. Sci. USSR Press, 1949).
- [6] D. Josefowitz and H. Mark, Indian Rubber World 106, 33 (1942).
- [7] S. S. Voyutsky and V. M. Zamazy, Colloid J. 15, 407 (1953);\* Proc. Acad. Sci. USSR 81, 64 (1951).
- [8] S. S. Voyutsky and B. V. Shtrakh, Colloid J. 16, 3 (1954);\*\*Proc. Acad. Sci. USSR 90, 573 (1953).
- [9] A. I. Shapovalova, N. A. Tsvetkova and S. S. Voyutsky, Symposium, Scientific-Research Work of Central Scientific Leather Research Inst. 1953, p. 58.\*\*\*
- [10] B. V. Deryagin, S. K. Zherebkov and A. M. Medvedeva, Colloid J. 18, 404 (1956).\*
- [11] T. I. Sogolova and V. A. Kargin, Theses of Reports, Ninth Conference on the General Problems of the Chemistry and Physics of High Molecular Compounds (Acad. Sci. USSR Press, 1956), p. 127.\*\*\*

Received April 10, 1957

The All-Union Scientific-Research Institute for Aviation Materials

\* Original Russian pagination. See C. B. translation.

\*\* See C. B. translation.

\*\*\* In Russian.

# THE ROLE OF HYDROGEN ATOMS IN THE REACTION OF CATALYTIC OXIDATION OF HYDROGEN ON PALLADIUM

V. B. Kazansky and V. V. Voevodsky

(Presented by Academician N. N. Semenov, April 12, 1957)

Despite the fact that the reaction of catalytic oxidation of hydrogen on the metals of the platinum group has been studied by a great number of authors, the mechanism of this reaction is still unclear at the present time. It is not even clear whether the reaction proceeds according to a chain [1-3], a radical [4-6] or a molecular [2, 7] mechanism. Ionic mechanisms are also possible [8]. In the work of Wagner and Hauffe [2] the mechanism of the catalytic oxidation of hydrogen on metallic palladium was studied by comparing the equilibrium concentration of atomic hydrogen with the stationary concentration on the catalyst surface during the reaction. The authors arrived at the conclusion that a chain mechanism was possible for this reaction. The question of chain mechanisms in heterogeneous catalysis has recently been subjected to a detailed theoretical consideration in a number of papers. In this connection it seemed to us to be of interest to independently confirm the conclusions of Wagner and Hauffe by using a different experimental method.

According to modern conceptions, the adsorption and dissolution of hydrogen in metallic palladium is accompanied by the dissociation of hydrogen molecules on the metallic surface and the formation of adsorbed hydrogen atoms. The dissolving and diffusion of hydrogen into the depths of the metal clearly involves hydrogen in ionic form [9]. At equilibrium the concentration of the atomic hydrogen adsorbed on the metallic surface can be determined from the equality between the rates of the processes of dissociation and recombination on unit surface.

$$W_{\text{diss}} = K_r [H_{\text{eq}}]^2. \quad (1)$$

Here  $K_r$  is the constant for recombination and  $H_{\text{eq}}$  is the equilibrium concentration of the adsorbed hydrogen atoms. In the molecular reaction mechanism for the catalytic oxidation of hydrogen on a palladium surface, hydrogen atoms are not consumed by the reaction. Thus despite the fact that the total amount of atomic hydrogen on the catalytic surface is diminished as a result of the adsorption of oxygen, the concentration of hydrogen atoms on the free positions will be that corresponding to equilibrium. In the radical reaction mechanism two hydrogen atoms are consumed in the formation of each water molecule and for the part of the surface which is not occupied by oxygen Eq. (1) can be written in the form:

$$W_{\text{diss}} = K_r [H_{\text{stat}}]^2 + W_{\text{ox}}, \quad (2)$$

$H_{\text{stat}}$  being the stationary concentration of hydrogen atoms on the catalyst surface. In the course of the reaction according to a nonbranching chain mechanism with a chain length  $\nu$ , the entrance of one initial hydrogen atom into the reaction leads to the formation of  $\nu$  water molecules. In conformity with this and with rupture of the chain on oxygen, the equation of balance for the hydrogen atoms can be written in the following form:

$$W_{\text{diss}} = K_r [H_{\text{stat}}]^2 + \frac{W_{\text{ox}}}{\nu}. \quad (3)$$

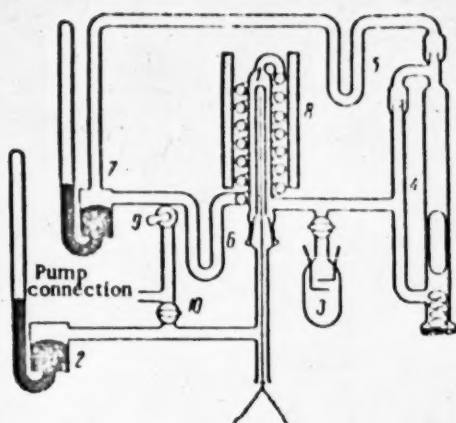


Fig. 1. A diagram of the apparatus.

and for a nonbranching chain mechanism with a second power chain rupture:

$$\frac{H_{\text{stat}}}{H_{\text{eq}}} = 1. \quad (6)$$

It can be shown that in the course of the reaction with a branching chain mechanism, the concentration of the atomic hydrogen must be greater than the equilibrium concentration. From what has been said it follows that certain conclusions concerning the reaction mechanism can be drawn by comparing the stationary concentration of atomic hydrogen on the catalyst surface with the equilibrium concentration.

Such comparison for the atomic hydrogen which is adsorbed on palladium has been carried out in our experiments with the aid of a diffusional process. The experiments were performed in a circulating vacuum system which made it possible to carry out the reaction under stationary conditions [10] (Fig. 1). The catalyst was the palladium cylinder 1, on the external surface of which the reaction took place. The magnitude of the catalyst surface was about 15 cm<sup>2</sup>. The interior of the capillary was connected with the manometer 2, which was read with the aid of a cathetometer. The mixture of hydrogen and oxygen was circulated by the glass circulating pump 4, the water which was formed as a result of the reaction being frozen out in the traps 5 and 6 which were

TABLE 1

Temperature, °C	Rate of reaction, mm of Hg per min	Partial pressure of O <sub>2</sub> , mm of Hg	Partial pressure of H <sub>2</sub> , mm of Hg	Stationary pressure of H <sub>2</sub> inside the capillary, mm of Hg
		In the reaction zone		
220	9	50	100	94
190	4.2	49	101	89
180	2.5	51	98	78

cooled by solid carbon dioxide. The volume of the circulation circuit of the gases was about 400 cm<sup>3</sup>. The loss of reagents resulting from the reaction was compensated by the electrolyzer 3. The electrolysis current was so selected that the total pressure, as measured by the manometer 7, remained constant over the course of the reaction. The stationary reaction velocity was indirectly determined through the magnitude of the electrolysis current.

The experiments were carried out in the following manner. On opening the cocks 9 and 10 which connect the interior of the capillary with the circulating gas circuit, hydrogen was emitted into the evacuated measuring section of the apparatus. The catalyst was maintained in hydrogen until the process of the dissolving of the

If the chain rupture occurs by recombination of the hydrogen atoms, Eq. (3) goes over into Eq. (1). Starting from Eqs. (1), (2) and (3) it is possible to derive expressions for the ratio between the stationary and the equilibrium concentrations of atomic hydrogen on the free portion of the catalyst surface for a radical reaction mechanism:

$$\frac{H_{\text{stat}}}{H_{\text{eq}}} = \sqrt{\frac{W_{\text{diss}} - W_{\text{ox}}}{W_{\text{diss}}}} \quad (4)$$

for a nonbranching chain reaction mechanism with chain rupture of the first order:

$$\frac{H_{\text{stat}}}{H_{\text{eq}}} = \sqrt{\frac{W_{\text{diss}} - \frac{W_{\text{ox}}}{\nu}}{W_{\text{diss}}}} \quad (5)$$

TABLE 2

Temperature, °C	Reaction rate, mm of Hg per min	$W_{diss} =$ $= 2W_{H/D}$	$\frac{P_{stat}}{P_{part}} = \frac{[H]_{stat}^2}{[H]_{eq}^2}$ (experimental)	$\frac{W_{diss} - W_{ox}}{W_{diss}}$ (theoretical)
220	9	115	0.94	0.91
190	4.2	32	0.88	0.87
180	2.5	18	0.80	0.86

hydrogen in the palladium was completed. Cock 10 was then closed, the hydrogen was pumped out from the communicating line and oxygen was introduced into the circulating circuit of the apparatus. Following this the circulations of the gas was commenced with the closing of cock 9 and the electrolyzer circuit was closed. It was observed that despite the equality of the partial pressures inside and outside of the capillary, there was a diffusion of hydrogen through the capillary walls in the direction of the reaction mixture. This diffusion process continued until a stationary condition was established. Thus the hydrogen pressure inside of the capillary corresponded to the stationary concentration of atomic hydrogen on the surface of the catalyst during the reaction. The diminution of the equilibrating hydrogen pressure during the establishment of a stationary condition when compared with the partial pressure of the hydrogen in the reaction zone served as a measure of the deviation of the stationary atomic hydrogen concentration from the equilibrium value. The results of certain of our experiments are presented in Table 1. From Table 1 it is to be seen that the stationary concentration of atomic hydrogen in the reaction zone is considerably less than the equilibrium concentration, this indicating that the atomic hydrogen is consumed during the oxidation reaction. For a more detailed investigation of the reaction mechanism we have carried out a calculation for the radical reaction mechanism (Eq. (4)) of the departure of the stationary concentration of atomic hydrogen on the catalyst surface from the equilibrium concentration and have compared the calculated values with the experimental. The rate of dissociation of hydrogen on the palladium surface was determined by us from the rate of the exchange of hydrogen with deuterium, a reaction which takes place through the dissociation of hydrogen molecules on the catalyst surface with subsequent recombination of the hydrogen atoms [11]. It was shown in special experiments that oxygen only slightly (up to 10-20%) lowers the rate of exchange reaction and, consequently, does not alter the mechanism of this reaction. In Table 2 there are presented the results of calculations in which this detail was taken into account. The good agreement between the experimental measurements and the calculated values points to a radical reaction mechanism for the oxidation of the hydrogen on metallic palladium under the condition studied by us. It should be noted that the calculation shows that under our conditions even short chains (5-6 steps) would lead to practical coincidence of the stationary and the equilibrium concentrations of atomic hydrogen.

Thus in distinction from Wagner and Hauffe, and from those other authors who have presumed the participation of molecular hydrogen in the catalytic oxidation of hydrogen on metals of the platinum group, our data uniformly points to the fact that, in the case of palladium, reaction occurs through the interaction of oxygen with the atomic hydrogen which is adsorbed on the catalyst surface.

#### LITERATURE CITED

- [1] R. P. Donnelly and C. N. Hinshelwood, *J. Chem. Soc.* 1929, 1727.
- [2] C. Wagner and K. Hauffe, *Zs. Elektrochem.* 45, 409 (1939).
- [3] G. K. Borekov, *J. Chim. Phys.* 51, 759 (1954).
- [4] I. Langmuir, *Trans. Farad. Soc.* 17, 621 (1922).
- [5] T. Tuchsolski, *Zs. Phys. Chem. B* 40, 333 (1938).
- [6] S. Yu. Elovich and V. S. Rozing, *Problems of Kinetics and Catalysis* [in Russian], No. 3 (Leningrad, 1937), p. 499.
- [7] R. P. Donnelly, *J. Chem. Soc.* 1929, 2438.

- [8] O. V. Krylov and S. Z. Roginsky, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1956, 145.\*
- [9] R. Berrer, *Diffusion in Solid Bodies* [in Russian] (Foreign Lit. Press, 1948), p. 172.
- [10] G. K. Borekov, M. G. Slinko and A. G. Filippova, *Proc. Acad. Sci. USSR* 92, 2, 353 (1953).
- [11] V. B. Kazansky, R. E. Mardaleishvili, V. P. Strunin and V. V. Voevodsky, *J. Phys. Chem.* 30, 4, 821 (1956).

Received April 5, 1957

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of Sciences of the USSR

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\* Original Russian pagination. See C. B. translation.



# THE RHEOLOGICAL PROPERTIES OF SURFACE FILMS AT THE OIL-WATER INTERFACE AND THEIR ROLE IN STABILIZING OIL EMULSIONS

M. M. Kusakov and A. A. Petrov

(Presented by Academician A. V. Topchlev, April 15, 1957)

Oil emulsions possess a high stability which is related to the formation of protective surface films on the drops of emulsifying water, these films possessing enhanced structural and mechanical properties which hinder the aggregation and fusion of the droplets [1]. For investigating the rheological properties of surface films at the oil-water interface an apparatus of the torsion pendulum type was employed. In measurements with such an

apparatus the surface film is inseparable from the bulk phases and for this reason it is necessary to introduce corrections for the viscous resistance of these phases in determining the rheological characteristics of the surface films. The results which have been obtained in the study of the surface properties of films at the oil-water interface show that it is possible, depending on the compositions of the hydrocarbon and the aqueous phases, the time of formation of the film, the temperature and other factors besides, to distinguish three types of movement of the torsion pendulum, namely: a) damped vibration, b) aperiodic movement and c) elastoviscous movement. The most complete information concerning the rheological properties of surface films is to be obtained from observations of the elastoviscous movement of the torsion pendulum.

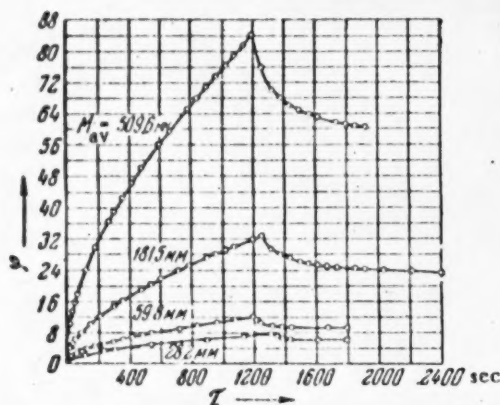


Fig. Curves showing the deformation,  $\varphi$ , of the surface film at the Mukhanov oil-sodium chloride solution (15% NaCl, pH 6.4) interface at various values of the torque,  $M_{av}$ . Experimental temperature 20-21°, holding time, 6.1-7.7 hours.

apparatus the surface film is inseparable from the bulk phases and for this reason it is necessary to introduce corrections for the viscous resistance of these phases in determining the rheological characteristics of the surface films. The results which have been obtained in the study of the surface properties of films at the oil-water interface show that it is possible, depending on the compositions of the hydrocarbon and the aqueous phases, the time of formation of the film, the temperature and other factors besides, to distinguish three types of movement of the torsion pendulum, namely: a) damped vibration, b) aperiodic movement and c) elastoviscous movement. The most complete information concerning the rheological properties of surface films is to be obtained from observations of the elastoviscous movement of the torsion pendulum.

In Fig. 1 typical curves are presented which show for surface films at an oil-water interface the development of film deformation as a function of time at various values of the torque. Analysis of these curves shows that the development of deformation in surface films at the oil-water interface proceeds similarly to the development of deformation in adsorbed films of saponin [2] and in bulk structured systems [3, 4]. Deformation vs time curves of such form can result from the simultaneous development of three types of deformation: instantaneous elastic deformation, deformation due to elastic after-effects and irreversible flow deformation. In conformity with this the rheological properties of surface films at the oil-water interface can be characterized by: the viscosity,  $\eta$ , of irreversible flow; the modulus,  $E_0$ , of instantaneous deformation; the modulus,  $E_p$ , of the elastic after-effect; the total modulus,  $E_m$ , of elastic deformation, defined by the equation:  $E_m^{-1} = E_0^{-1} + E_p^{-1}$ ; the conventional viscosity,  $\eta_p$ , of the elastic after-effect and the relaxation time,  $\theta_p$ , for the elastic after-effect. A static elastic limit below which the deformation might be completely reversible is not met, as a rule, in surface films at the oil-water interface, this same having also been observed in the adsorbed layers at the interface between saponin solutions and air [2].

TABLE 1

The Physicochemical Properties of Eastern Oils and the Rheological Properties of Their Surface Films at the Interface with an NaCl Solution (15%) at a Temperature of 20°; Time of Formation of the Films, 16-24 Hours and pH of the Aqueous Solution, 6.3-7.0

Oil	Production horizon	Physicochemical prop.					Elastoviscous prop. of films					Relaxation time of elastic after-effect, $\theta$ , sec
		Density, $\rho_4$ , g/cm <sup>3</sup>	Kinematic viscosity, $\nu$ , stokes	composition in wt. %			viscosity, surface poises		modulus, dynes/cm			
				silica gel	tan	asphalts	irreversible flow, $\eta$	elastic after-effect, $\eta_p$	instantaneous, $E_0$	elastic after-effect, $E_p$	total, $E_m$	
Zolnin Shkapov	Devon	0.7993	3.1	2.16	0.26	4.87	12800	8700	38	65	24	130
	Devon (Stratum IV)	0.8167	8.2	6.61	1.26	—	980	230	1.1	1.8	0.7	138
Bavlin Mukhanov	Devon	0.8368	7.9	7.58	1.75	5.62	11100	4200	36	16	11	250
	Carbonif. (Stratum I)	0.8485	11.8	7.12	1.60	7.5	1020	500	8.3	2.6	2.0	300
Tulmazin Kalinov Radaev	Devon	0.8493	10.6	7.32	1.56	~7	6700	5700	10	33	12	175
	Perm	0.8812	19.5	9.38	2.39	3.54	31	—	—	—	—	—
	Devon	0.9043	165	26.0	4.3	4.9	4100	4000	38	21	13.5	190

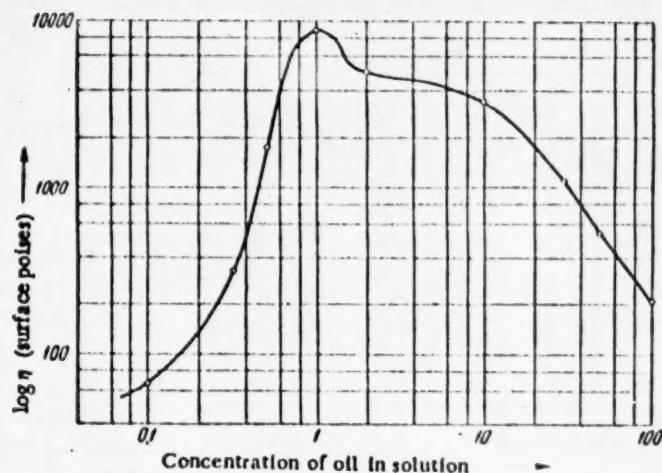


Fig. 2. Isotherms of the surface viscosity,  $\eta$ , of solutions of Romashkin oil at the interface with water. Experimental temperature 20°, holding time 4.0-4.5 hours.

In order to investigate the influence of the oil on the properties of the surface films, the rheological characteristics of surface films at the interface with 15% solutions of NaCl (pH 6.3-7.0) were studied for a number of oils of Eastern origin. The results obtained are given in Table 1.

The relation between the rheological properties of the surface films and the concentration of the polar fraction of the oil and the other components which enter in the formation of these films was studied for films of Romashkin oil at the interface with distilled water. In order to diminish the concentration of polar substances, this oil was diluted with an isoviscous mixture of vaseline and nonpolar kerosene. An isotherm (in logarithmic coordinates) of the surface viscosity over the interval of concentrations from 0 to 100% is presented in Fig. 2.

Corresponding to the maxima in surface viscosity, the surface films show elastic properties over the concentration interval from 0.5 to 10%; isothermal curves of these properties are sketched in Fig. 3, along with isotherms for the viscosity of irreversible flow at various torques.

The surface films of the various oils at the oil-water interface possess high elastoviscous properties: the magnitude of the surface viscosity reaches a value of the order of  $10^4$  surface poises. A comparison of the general physicochemical properties of the oils (density, viscosity, content of tars and asphalts) and the rheological properties of the surface films at the interface with water shows that, although an increase of the density and viscosity is accompanied by an increase in the concentration of the asphalt-tarry substances which are basic components of the surface films, the alteration of the elastoviscous properties of these layers does not proceed in parallel with the change of the concentration of these asphalts and the tars. The absence of such a relation is obviously tied up with the fact that the strength of these films is determined in the first instance, not by the absolute concentration in the oil of those components which enter into the make-up of the film, but by the physicochemical properties of the latter. It is for this reason that the more "heavy" oils (Kalinov, Radaev) form layers which are less viscous and stable than those of the "lighter" oils (Zolnin, Bavlin, Tulmazin). The isotherms for the elastoviscous properties of surface films of solutions of Romashkin oil at the interface with water (Figs. 2 and 3) show sharply defined maxima at oil concentration of 1-2%.

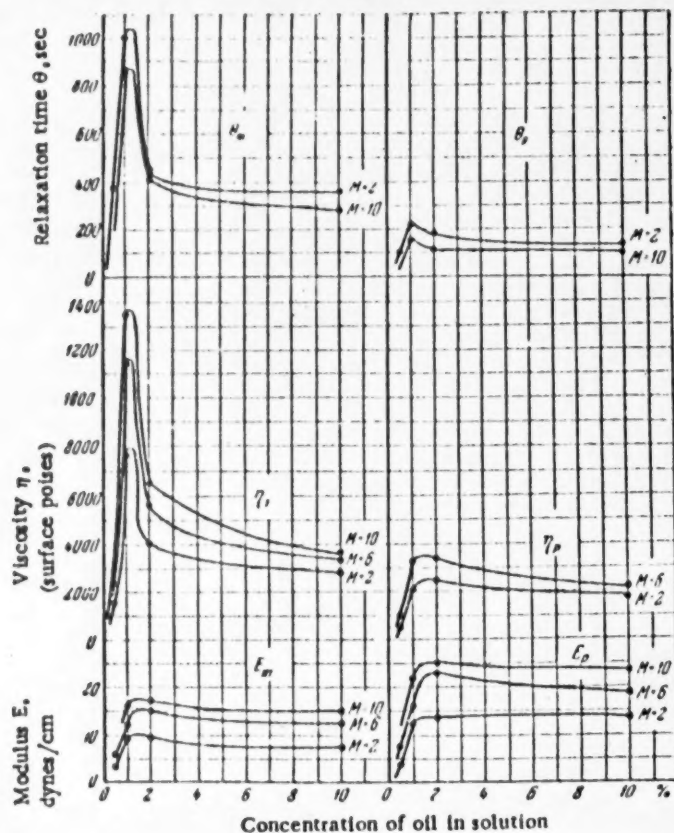


Fig. 3. Isotherms of the relaxation times for stresses,  $\theta_m = \eta/E_m$  and for elastic after-effects,  $\theta_p = \eta_p/E_p$ ; of the surface tensions for irreversible flow,  $\eta_i$ , and for elastic after-effects,  $\eta_p$ ; of the moduli of total elasticity,  $E_m$ , and of elastic after-effect,  $E_p$ , for surface properties of solutions of Romashkin oil at the interface with water at various values of the torque,  $M$ . Experimental temperature  $20^\circ$ , holding time 4.0-4.5 hours.

The appearance of maximum strength in surface films at the interface with water in the region of diluted oil solutions is clearly related to the more intensive gelatization of the asphalt-tarry substances in the surface layer which results from the dilution of the oil with a nonpolar solvent containing few aromatic compounds, it being known [1] that hydrocarbons of the saturated and the naphthalene series are coagulents for asphalt-tarry substances whereas aromatic hydrocarbons peptize these latter. In addition, the dilution of the oil with a nonpolar solvent diminishes the concentration of the asphalts and tars in the mixture which clearly aids in the formation of microcrystals of paraffin, the crystallization of which is retarded by the asphalt-tarry substances. Dilution at the same time diminishes the concentration in solution of those substances which enter in the make-up of the film and this must lead to a diminution of the stability. As a result, the strength of the film increases at the beginning of the dilution of the oil with a nonpolar solvent, reaches a maximum, and then rapidly diminishes. To this decrease in the values of the parameters of the elastoviscous properties of the surface film there must be at the oil-water interface a corresponding diminution in the concentration of surface active substances (acids, tars, asphalts, etc.) and also of the other components (microcrystals of paraffin, mineral particles, etc.) which assure stability for the surface. This must occur over a region which is far removed from the saturation concentrations of the film components, as is the case with solutions of Romashkin oil for which the decrease in viscosity and film stability occurs at concentrations from 0 to 1% whereas saturation of the layer with surface active substances corresponds to a concentration of approximately 8%.

The investigation of the influence of the composition of the oil and the water phases, the temperature, the time of formation of the film and other factors, on the rheological properties of surface films makes it possible to justify the selection of methods for dehydration and salt elimination in a given oil, to characterize its parameters and to evaluate the effectiveness of the action of emulsifiers.

#### LITERATURE CITED

- [1] L. G. Gurych, The Scientific Basis of the Treatment of Petroleum [in Russian] (Moscow-Leningrad, 1940); P. A. Rebinder, Bull. Acad. Sci. USSR, Div. Exptl. Medicine, chem. ser. No. 5, 639 (1936); Colloid J. 8, 157 (1946); P. A. Rebinder and K. A. Pospelova, "Modern concepts of the stability, formation and disintegration of emulsions," introductory article in the book by V. Kletton, Emulsions [in Russian] (Foreign Lit. Press, 1950).
- [2] A. A. Trapeznikov, J. Phys. Chem. 12, 583 (1938); 13, 406 (1939); 20, 61 (1946); Proc. Acad. Sci. USSR 63, 67 (1948); Colloid J. 12, 67 (1950); P. A. Rebinder and A. A. Trapeznikov, J. Phys. Chem. 12, 573 (1938); A. A. Trapeznikov, Trans. Inst. Phys. Chem., Acad. Sci. USSR 1, 120 (1950); A. A. Trapeznikov, Conf. on Viscosity of Liquids and Colloidal Solutions, Acad. Sci. USSR 1, 67 (1941).
- [3] P. A. Rebinder and E. E. Segalova, Proc. Acad. Sci. USSR 71, 85 (1950); Colloid J. 10, 223 (1948); 13, 461 (1951).
- [4] G. V. Vinogradov and K. P. Klimov, Proc. Acad. Sci. USSR 57, 911 (1947); 58, 1677 (1947); 71, 307, 701 (1950); J. Tech. Phys. 18, 355 (1948); Petroleum Economy No. 12, 47 (1947); No. 1, 52 (1948); G. V. Vinogradov et al., Colloid J. 18, 633 (1956).\*

Received February 28, 1957

The Petroleum Institute of the Academy of Sciences  
of the USSR

\* Original Russian pagination. See C. B. translation.



## THE INTERMEDIATE PRODUCTS IN THE OXIDATION-REDUCTION PHOTOREACTIONS OF THE XANTHENE DYES

V. F. Tsepalov and I. Ya. Shlyapintokh

(Presented by Academician A. N. Terenin, April 12, 1957)

The xanthene dyes, eosin, erythrosine and Bengal rose are frequently employed as photosensitizers in processes of oxidation and polymerization. According to the generally accepted view, photosensitization is realized in such processes by means of cyclic oxidation-reduction reactions of the dye with the components of the system. At the end of each cycle the dyestuff is regenerated and in the system there arise either end products or intermediate compounds which do not contain the dyestuff in their make-up.

The potentiometric method has been employed for studying the reactions of photo-oxidation and photo-reduction in the xanthene dyestuffs, the applicability of this technique to the study of oxidation-reduction photoreactions having been convincingly proven over recent years by the work of the Laboratory of Photobiochemistry of the Institute of Biochemistry of the Academy of Sciences of the USSR on the photo-reduction of chlorophyll, its analogs and related compounds [1]. The measurement of the kinetics of the change in the potential of an inert electrode which was immersed in an illuminated solution containing the pigment and a reducing agent, together with the measurement of photoconductivity, made it possible in this earlier work to establish the stepwise nature of the reduction process and to reveal the existence of the very active intermediate product of this reaction. In our work the measurement of the photogalvanic effect has permitted us to detect the formation of intermediate products in the oxidation-reduction reactions of a series of dyes. It should be also noted that the clearly expressed stepwise nature of this process opens the possibility for utilizing in its study the new methods which have been proposed by N. M. Emanuel [3] for the investigation of complicated reactions (by changing the conditions and the interactions during the course of the process).

These experiments were carried out in a vessel equipped with platinum electrodes, the construction of which has been described in [1b]. One of the arms of this vessel was blackened and the other illuminated by a SVDS-250 lamp. The rays from this lamp were focused with a condenser, passed through a cell with a  $\text{CuSO}_4$  solution, a SZS-14 thermo-filter and the light filters ZhS-11, ZhS-18 and SZS-18 which separated out the region 500-550 m $\mu$ . The vessel was placed at the focus of the light source in a transparent Dewar flask filled with methanol. The photopotentials were measured with a lamp potentiometer of the LP-5type.

In complete agreement with the results which have been obtained with chlorophyll, pheophytin and other pigments, we have established that the illumination of alcohol or pyridine solutions of the xanthene dyestuffs ( $C = 10^{-6}$ - $10^{-3}$  moles/liter) in the presence of oxygen, leads to a displacement of the electrode potential in the positive direction whereas in the presence of a reducing agent (alcohol, pyridine, ascorbic acid, aldehyde), illumination displaces the electrode potential in the negative direction. For the investigated cases these experiments indicate that the sign of the photopotential is determined in a dye-oxygen system by the oxidation products and in a dye-reducing agent system by the reduction products. In Fig. 1 there are presented kinetic curves for the change in the potential of a platinum electrode immersed in a pyridine solution of eosin which contained ascorbic acid as a reducing agent. These measurements were carried out at light intensities ranging from  $I = 1$  to  $I = 0.08$ . As is to be seen from these curves, the electrode potential falls during illumination, reaches a definite minimum, and then once more rises, returning to the initial value. By the time the potential of the illuminated electrode has again taken on the initial value, the eosin is fully decolorized. If the light is cut off at any point during the change of the potential, a displacement of the potential in the direction of negative values results. Addition of oxygen

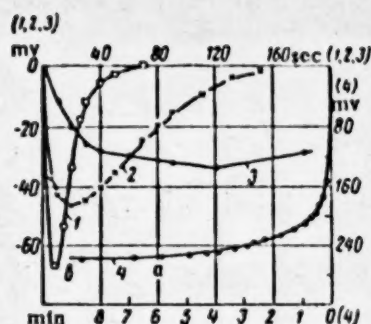


Fig. 1. The kinetics of the change of potential at various light intensities and concentrations of eosin. Reducing agent—ascorbic acid ( $1.2 \cdot 10^{-2}$  moles/liter). 1)  $I = 1$ ,  $C_e = 4 \cdot 10^{-6}$  moles/liter; 2)  $I = 0.32$ ,  $C_e = 4 \cdot 10^{-6}$  moles/liter; 3)  $I = 0.08$ ,  $C_e = 4 \cdot 10^{-6}$  moles/liter; 4)  $I = 1$ ,  $C_e = 4 \cdot 10^{-5}$  moles/liter.

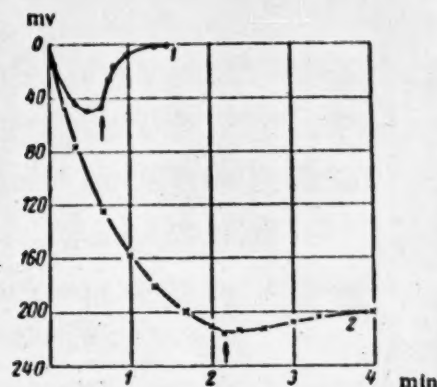


Fig. 2. The kinetics of the change in potential in pyridine at various temperatures. Reducing agent—ascorbic acid ( $1.2 \cdot 10^{-2}$  moles/liter). 1)  $C_e = 4 \cdot 10^{-6}$  moles/liter,  $t = 21^\circ$ ; 2)  $C_e = 4 \cdot 10^{-6}$  moles/liter,  $t = -33^\circ$ . The arrows indicate the instant of cutting off the illumination.

displaces the electrode potential in the same direction. The change in potential resulting from oxygen addition is, however, much more rapid. To the change of potential resulting either from cutting off the light or from adding oxygen, there corresponds an increase in the adsorption of the initial dyestuff. Thus, either through cutting off the illumination or through the introduction of oxygen there is observed a complete, or partial, reversal of the reaction.

From the form of the kinetic curves (Fig. 1) it could be supposed that the observed alteration of the photopotential is related to the existence of an intermediate product. In the initial stage of the reaction, from its beginning up to the potential minimum, there occurs an accumulation of this intermediate product, which changes the electrode potential. At the minimum point the rate of formation of the intermediate product is equal to its rate of consumption. On the right branch of the curve, the diminution of the concentration of the initial dyestuff results in a rate of loss of the intermediate product,  $W_2$ , which is greater than the rate of its formation,  $W_1$ , and the potential therefore gradually increases. From this point of view there is also to be understood the dependence of the kinetics of the potential change on the light intensity. As is to be seen from Fig. 1, the initial rate of change in the potential is proportional to the intensity of the absorbed light,  $I_{abs}$ . Thus, at the higher values of  $I_{abs}$  the concentration of the intermediate product must reach higher values and the potentials are accordingly lower. In addition, with an increased rate of formation of the intermediate product at a fixed value of the velocity constant for its consumption, the minimum point must move toward the origin of coordinates. From Fig. 1 it is to be seen that this is actually observed in practice.

The considerations which have been outlined also explain the observed relation between the kinetics of the potential change and the concentration of the dye. An increase in the concentration of eosin leads to increased adsorption of light and, in general, acts on the kinetics of the process just as does an increase in the light intensity. The only exception is observed in that case in which the eosin taken is considerably in excess of that which is necessary for complete light absorption. In this instance (curve 4, Fig. 1), the potential also rapidly diminishes and then remains constant over an extended period of time. If it is considered that at a high initial concentration of the eosin the rate of formation of the intermediate compound remains unaltered until the solution absorbs all of the incident light, the change of potential can then be explained by the fact that on the segment ab there is set up a stationary concentration of this product.

With a decrease in the temperature there is a sharp diminution in the rate of recovery of the potential (Fig. 2). This rate remains very low even after cutting off the illumination. Thus, the relation between the kinetics of the potential change and the temperature clearly points to the stepwise nature of the reduction process. The step involving formation of the intermediate product is photochemical. Its rate does not depend on the temperature. The second stage calls for further reaction of the intermediate product and is a dark reaction requiring

thermal activation. It is to be seen from Fig. 2 that a decrease of the temperature markedly increases the extent of the fall of the potential and the displacement of the minimum point in the direction of longer times. These facts find their natural explanation in the framework of the above expressed considerations concerning the relation between the rates of formation and consumption of intermediate products.

Experiments in which the concentration of the reducing agent was altered indicate the participation of the latter in the reaction of consumption of the intermediate product. It is for this reason that the application of butanal, a weaker reducing agent than ascorbic acid, leads to a more gradual recovery of the potential to its initial value after passing through the minimum. The nature of the solvent strongly affects the rate of the reaction of the intermediate product with the reducing agent. Thus, in ethanol the first stage of the photoreaction of eosin with the reducing agent proceeds just as rapidly as in pyridine, whereas the second stage is much slower. In both of these solvents the intermediate product reacts more rapidly with ascorbic acid than with butanal.

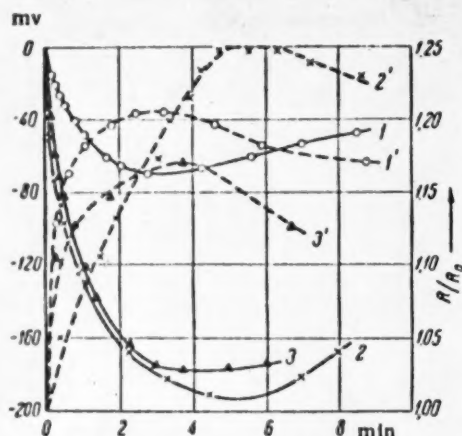


Fig. 3. The kinetics of the change of potential and resistance of solutions of dyes in pyridine. Reducing agent—butanal (0.1 moles/liter). 1, 2, 3) Potentials; 1', 2', 3') resistances; 1, 1') eosin; 2, 2') erythrosine; 3, 3') Bengal rose.

the temperature of the solution is lowered to  $-80$  or  $-90^\circ$ , no observable change in potential is observed during illumination and the dye is not decolorized. These experiments indicate that a slow photo-reduction of the dye-stuff by the solvent occurs in the absence of a reducing agent. The photochemical step requires a considerable energy of activation. Similar phenomena are also to be observed in the system pyridine—eosin. It should also be noted that the photochemical step in the reaction of reduction of eosin by butanol, a weak reducing agent, has a pronounced temperature coefficient.

In Fig. 3 there are presented curves showing the change of potential in the photoreactions of the reduction of eosin, erythrosine and Bengal rose by butanal in pyridine solution. It is to be seen from Fig. 3 that the kinetic curves are similar in all three of these dyestuffs. It can thus be considered that the first step in the photo-reduction of erythrosine and Bengal rose consists, just as in the photoreduction of eosin, in the formation of an intermediary product. The presence of intermediate products can be indicated by other methods as well, e. g., by measurement of the electroconductivity of the solution during the course of the reaction. The corresponding curves of Fig. 3 possess maximal values, a minimum in the potential being associated with a maximum in the resistance of the solution. Accordingly, the curves showing the change of potential and resistance describe the same process, namely, the formation and consumption of an intermediate product.

The kinetic curves which are obtained by illuminating solutions of xanthene dyes in the presence of oxygen are without maxima: the electrode potential gradually rises and after 20-30 minutes takes on a constant value. Measurements which were carried out on the reversibility of the reaction after cutting off illumination have shown

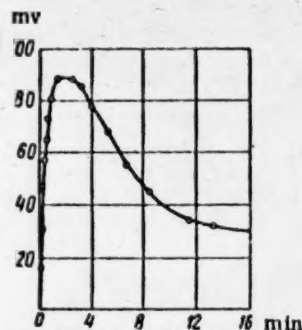


Fig. 4. The kinetics of the change of potential during photo-oxidation of chlorophyll by air in ethanol.

If a solution of eosin in ethanol is illuminated in the absence of a reducing agent and oxygen, there is also to be observed a fall of the potential during the illumination, the process proceeding considerably more slowly than in the presence of the reducer. In the course of extended illumination decolorization of the dyestuff is to be observed. After cutting off the illumination the potential very gradually returns to its initial value. If

that with short periods of illumination a considerable reversibility is to be observed whereas with longer periods the system becomes practically irreversible.

Differences in the reversibility of the photoreactions with short and with long periods of illumination have also been observed by us in the photo-oxidation of chlorophyll a + b, in the course of which a relatively stable intermediate product is formed (Fig. 4). This product was earlier detected by A. A. Krasnovsky using a spectral method [2]. Thus from the example of the reaction of photo-oxidation of chlorophyll it is clear that the difference in the reversibility can be explained by the formation of an intermediary product. However, measurements of the reversibility of the reaction of oxidation of eosin by the potentiometric method alone do not uniquely indicate the existence of an intermediate oxidation product of the dyestuff itself, since the process of decolorization is a complex one. In addition to the reaction of the dye with oxygen it can also involve sensitized oxidation of the solvent and reaction of the oxidation products of the solvent with the dye. Thus further investigations are needed to prove the existence of intermediate products in the oxidation of xanthene dyes.

#### LITERATURE CITED

[1] V. B. Evstigneev and V. A. Gavrilova: a) Proc. Acad. Sci. USSR 92, 381 (1953); b) 95, 841 (1954); c) 96, 1201 (1954); d) 98, 1017 (1954).

[2] A. A. Krasnovsky, Proc. Acad. Sci. USSR 58, 617 (1947).

[3] N. M. Emanuel, Annals Moscow State University, Vol. 174 (1955).

Received February 7, 1957



# SPECTROSCOPIC INVESTIGATION OF THE EQUILIBRIUM OF THE REACTION $\text{NaCl} \rightleftharpoons \text{Na} + \text{Cl}$ IN A HYDROGEN-CHLORINE FLAME AND THE ENERGY OF DISSOCIATION OF $\text{NaCl}$

L. V. Gurvich and I. V. Veits

(Presented by Academician V. N. Kondratyev, May 4, 1957)

In our previous papers [1-3] dealing with the determination of the energy of dissociation of  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{SrO}$ ,  $\text{BaO}$  and  $\text{AlO}$  we have used a method which is based on the determination of the partial pressure of the corresponding metal, introduced into the flame, from the absolute intensity of the lines due to the metal in the spectrum of the flame. In the case of investigations with flames burning in oxygen and air ( $\text{C}_2\text{H}_2 + \text{air}$ ,  $\text{C}_2\text{H}_2 + \text{O}_2$ ,  $\text{H}_2 + \text{O}_2$ , etc.) this method allows, as a rule, to determine only the energy of dissociation of the oxides of the metals, because in flames of this type most metals exist mainly in the form of their compounds with oxygen. Only in those cases where a metal does not form stable oxides can the energies of dissociation of compounds of metals with other products of combustion (in particular with the hydroxyl radical) also be determined by investigation of the spectra obtained in oxygen flames. It might be expected that a flame in which the oxidizing agent is a halogen would be a more suitable source of radiation for the spectroscopic investigation of the energies of dissociation of halogen compounds of metals. In order to demonstrate the possibility of determining the energies of dissociation of metal chlorides in a chloro-hydrogen flame we have in the present work investigated the energy of dissociation of  $\text{NaCl}$  which is known with sufficient accuracy [4]. The experimental arrangement for producing the  $\text{H}_2 + \text{Cl}_2$  flame is similar to that already described [1]. The only difference is in the method of introducing the solution of the Na-salt into the flame which in this case enters the flame not with the oxidant stream but with the hydrogen. Since chlorine reacts vigorously with mercury a double differential manometer with a buffer layer of concentrated sulfuric acid was used for measuring the consumption of chlorine.

The investigation was carried out in a flame fed by a fuel mixture composed of 1.00 parts of  $\text{H}_2$  + 0.80 parts of  $\text{Cl}_2$  + 0.016 parts of  $\text{H}_2\text{O}$  (liq.). The temperature of this flame calculated theoretically [5] without allowing for heat losses and assuming that the flame gases are in thermodynamic equilibrium and that the products of combustion contain only  $\text{Cl}$ ,  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{H}_2$ ,  $\text{H}$ ,  $\text{OH}$  and  $\text{H}_2\text{O}$ , is equal to 2450°K. The partial pressure of atomic chlorine under these conditions is equal to  $3.37 \cdot 10^{-2}$  atmos. The literature contains no record of any experimental investigations of the temperature of the  $\text{H}_2 + \text{Cl}_2$  flame. Our investigation of the temperature of the flame by the reversal of the sodium D-line at a height of 3-6 mm above the reaction zone showed that it lies in the range from 2350 to 2550°K. Since the chlorides of most metals have relatively high energies of dissociation, it is difficult to produce a high concentration of atoms of the corresponding metal in a chloro-hydrogen flame and a more accurate determination of the temperature of this flame by the reversal method is difficult (see [6]).

In the investigation of the equilibrium of the reaction  $\text{NaCl} \rightleftharpoons \text{Na} + \text{Cl}$  dilute solutions of two different salts of sodium ( $1.02 \cdot 10^{-3}$  N  $\text{NaCl}$  and  $1.19 \cdot 10^{-3}$  N  $\text{Na}_2\text{CO}_3$ ) were injected into the flame. The partial pressure of Na in the flame was determined from the absolute intensity of the resonance lines at 5890 and 5896 Å in the flame spectrum at a height of a few millimeters above the reaction zone. The method of measurement and the treatment of the experimental results has been described in [1]. It was assumed that the absolute probability of the transition of both lines was equal to  $6.25 \cdot 10^7 \text{ sec}^{-1}$  [7], and the effective width of the flame as determined from the transverse spectrogram was equal to 0.35 cm. The values of  $P_{\text{Na}}$  obtained from these investigations are given in Table 1. Values of  $P_{\Sigma \text{Na}}$ , that is, the sum of the partial pressures of sodium and of its compounds in the flame gases, are also given. The latter values are calculated from the concentration of the sodium salt introduced

into the flame, the composition of the fuel mixture feeding the flame and the composition of the flame gases. Using the values of  $P_{Na}$  and of the partial pressures of the component gases of the products of combustion of the chloro-hydrogen flame, it can be shown that under conditions of equilibrium Na exists in this flame almost exclusively in the form of NaCl,  $Na^+$  and Na and that the partial pressures of NaH, NaOH and  $Na_2Cl_2$  are negligible. Values of  $P_{Na^+}$  were calculated from the relation

$$P_{Na^+} = \sqrt{K_1 \left(1 + \frac{P_{Cl}}{K_2}\right) P_{Na}}$$

obtained from the system of equations:  $\frac{P_{Na^+} \cdot P_e}{P_{Na}} = K_1$ ,  $\frac{P_{Cl} \cdot P_e}{P_{Cl^-}} = K_2$  and  $P_{Na^+} = P_{Cl^-} + P_e$ . The values of  $K_1 = 2.63 \cdot 10^{-9}$  and  $K_2 = 1.377 \cdot 10^{-8}$  were calculated from the Saha equation. The values of  $P_{Na^+}$  calculated by this method are given in Table 1 which also includes values of  $P_{NaCl} = P_{\Sigma Na} - P_{Na^+} - P_{Na}$ , of the equilibrium constant of the reaction  $NaCl \rightleftharpoons Na + Cl$  at the temperature of the flame, and of  $D_0(NaCl) = T(\phi_{Na}^* + \phi_{Cl}^* - \phi_{NaCl}^* - R \ln K_p)$ .

TABLE 1

Values of  $P_{Na}$ ,  $P_{\Sigma Na}$ ,  $P_{Na^+}$ ,  $P_{NaCl}$  (in atmos) in the  $H_2 + Cl_2$  Flame and Values of  $D_0(NaCl)$  (in kcal/mole)

Salt solution	$P_{\Sigma Na} \cdot 10^9$	$P_{Na} \cdot 10^{10} *$	$P_{Na^+} \cdot 10^{10} **$	$P_{NaCl} \cdot 10^{10} **$	$K_p \cdot 10^8 **$	$D_0 **$
NaCl $1.02 \cdot 10^{-3} N$	1.58	$4.72 \pm 0.93$	$5.50 \pm 0.55$	$1.03 \pm 0.06$	$1.54 \pm 0.40$	$98.6 \pm 1.2$
$Na_2CO_3$ $1.19 \cdot 10^{-3} N$	1.85	$6.87 \pm 1.04$	$6.65 \pm 0.50$	$1.18 \pm 0.05$	$1.96 \pm 0.40$	$97.5 \pm 1.1$

\* Arithmetic means of results of 20 determinations of the intensity of two Na lines.

\*\* The errors indicated allow only for the scatter of individual determinations of the intensity of the sodium lines.

Values of the  $\phi^*$ -potentials of Na, Cl and NaCl necessary for these calculations were obtained by methods of statistical thermodynamics.

Allowing for the possible systematic errors inherent in our method (see [1]) the value of  $D_0(NaCl)$  obtained was equal to  $98.0 \pm 3.00$  kcal/mole, which is in excellent agreement with the value proposed by Gaydon [4] ( $97.6 \pm 1.3$  kcal/mole) and obtained from investigations of atomic fluorescence and from determinations of the heat of sublimation. The mutual agreement of the results obtained with solutions of two different salts as well as the agreement of these results with those obtained by other methods allows us to assume that the conditions existing in the external cone of the flame are close to equilibrium conditions and shows that the energies of dissociation of metal chlorides can be investigated in the chloro-hydrogen flame.

#### LITERATURE CITED

- [1] I. V. Veits and L. V. Gurvich, Optics and Spectroscopy 1, 1, 26 (1956).
- [2] I. V. Veits and L. V. Gurvich, Proc. Acad. Sci. USSR 108, 4, 659 (1956).
- [3] I. V. Veits and L. V. Gurvich, J. Phys. Chem. 31, 10 (1957).
- [4] A. Gaydon, Dissociation Energy and Spectra of Diatomic Molecules (London, 1953).
- [5] V. Iost, Explosions and Combustion in Gases (Foreign Literature Press, 1952) [Russian translation].
- [6] A. G. Sviridov and N. N. Sobolev, J. Exptl.-Theoret. Phys. 24, 1, 93 (1953).
- [7] L. S. Mandelshtam, Introduction to Spectroscopic Analysis (Moscow, 1946).\*

Received April 25, 1957

\* In Russian.

## THE EFFECT OF THE DEGREE OF ELONGATION ON OZONE CRACKING OF RUBBERS

Yu. S. Zuev and S. I. Pravednikova

(Presented by Academician P. A. Rebinder, June 6, 1957)

It is known from the literature that there exists a so-called critical elongation at which disruption of the structure of rubbers under the influence of ozone is most severe. However, the available data concerning this problem are fairly contradictory.

According to a number of statements the critical elongation is observed in the case of vulcanizates of natural rubber, but its estimation by different authors varies from 5 to 50% [1-4]. Some authors consider that a critical elongation exists in the case of synthetic rubbers susceptible to attack by ozone [1], while others consider that no such characteristic exists [5, 6]. It is said that polychloroprene and butyl rubber do not possess this characteristic [1, 7]. However, none of these data can be regarded as reliable since in most cases ozone cracking of the rubbers was characterized by arbitrary methods, as a rule by the "degree of cracking" expressed by the number of marks.

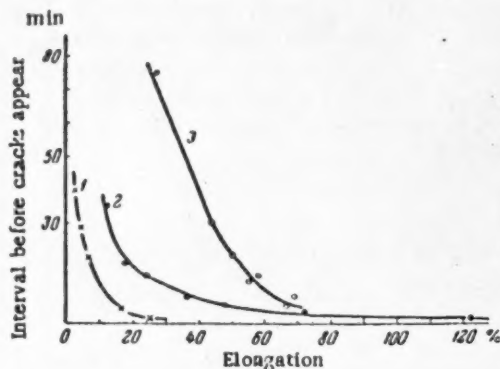


Fig. 1. Effect of the degree of elongation on the time preceding the appearance of cracks: 1) Compound NK, ozone concentration 0.0033%; 2) compound SKS-30, ozone concentration 0.0027%; 3) neurite, ozone concentration 0.010%.

We have carried out a detailed investigation of the effect of the degree of elongation on ozone cracking of rubbers, the rate of growth of cracks being determined by an objective method [8] based on the effective depth of the cracks calculated from the decrease of stress in the relaxed rubber sample when exposed to the action of ozone. The following rubber compounds were investigated at their optimum true tensile strength: rubbers NK, SKS, neurite, SKN, SKB (standard formulas), guttapercha (elastic vulcanizate) and butyl rubber.\*

The investigation has produced the following information:

1. The same qualitative dependence of the time interval preceding the appearance of cracks on the degree of elongation is found in the case of all the rubbers: with increasing percentage elongation the time interval preceding the appearance of cracks gradually decreases to zero (Fig. 1).

2. The rate of growth of the cracks determined in the stationary region of the kinetic curve increases at first with increasing elongation, passes through a maximum in the region of small percentage elongations ("critical elongation"), and subsequently decreases for elongations of up to 500% (Fig. 2a).

\* Composition of rubbers: guttapercha 100 parts, captax 0.8 parts, sulfur 5 parts, butyl rubber 100 parts, stearine 3 parts, captax 0.65 parts, thiuramdisulfide 1.3 parts, zinc oxide 5 parts, sulfur 2 parts.

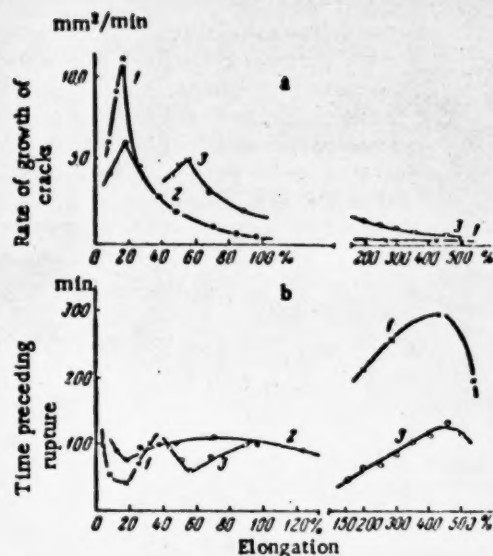


Fig. 2. Dependence of the rate of growth of cracks (a) and of the time interval preceding rupture (b) on percentage elongation: 1) compound NK, ozone concentration 0.003%; 2) compound SKS-30, ozone concentration 0.002%; 3) neurite, ozone concentration 0.01% (at small elongations) and 0.02% (at large elongations).

3. In the case of all the rubbers, irrespective of their properties, the time interval necessary to achieve rupture of the specimen at different percentage elongations passes through a minimum in the region of the critical elongation,  $\epsilon_{min}$ , and through a maximum in the region of larger percentage elongations (Fig. 2b).

Undoubtedly the most interesting results established by our objective method in the case of all the rubbers investigated is the reinforcing effect obtained in the strained rubbers as a result of which the rate of growth of the cracks decreases at elongations greater than the critical elongation  $\epsilon_{min}$ , while the time interval preceding rupture of the samples increases.

From the point of view of existing ideas about the nature of ozone cracking of rubbers as a process which is determined by the chemical interaction of the rubber with ozone, it was natural to expect that stretching would have an activating effect on the disruption of rubber under the influence of ozone, but never the opposite effect.

Earlier we have suggested [9] that this phenomenon, in spite of the marked increase in the rate of the process, is analogous to static fatigue. The direct experiments have also established a straightforward relationship between the strength of the rubbers and their resistance to cracking under the influence of ozone. The greater the true strength of rubbers compounded from noncrystallizing polymers, the greater is their resistance to ozone cracking, as is shown by the following data:

Rubber based on compound SKB, stress 2 kg/cm<sup>2</sup>, concn. of O<sub>3</sub> = 2.2 · 10<sup>-3</sup>%

True tensile strength, kg/cm <sup>2</sup>	8.6	247	516	758	830
Time interval preceding rupture, min	25	54	86	105	116

Rubber based on compound SKS-30, stress 2.5 kg/cm<sup>2</sup>, concn. of O<sub>3</sub> = 2.5 · 10<sup>-3</sup>%

True tensile strength, kg/cm <sup>2</sup>	346	401	430	757
Time interval preceding rupture, min	15	17	19	23

In the case of rubbers compounded from crystallizable rubber polymers a marked anisotropy of tensile strength is observed in the region of comparatively large percentage elongations: the strength measured in the direction of the stretching force is less than at right angles to it. When such rubbers are exposed to the action of ozone the formation of cracks is observed to occur in the direction of least tensile strength (longitudinal cracks), in preference to transverse cracks, as is usual (Fig. 3).

Examination of a rubber based on compound NK for resistance to ozone cracking after preliminary repeated stretching up to 110% elongation for a period of four hours has shown that the tensile strength of this rubber decreased by about 25% while the time interval preceding rupture in an ozone atmosphere decreased by 25-30%.

The effect of the mechanical strength of the rubbers on ozone cracking can be explained if we picture the process as taking place in two stages. 1. Ozone interacts with the polymer through the double bonds. It is clear that since the double bonds are not spaced symmetrically opposite one another, this interaction and, consequently, the "chemical" growth of a crack is terminated rapidly. 2. Along the edges of a crack there comes into play excess stress which induces further "mechanical" growth of the crack without the participation of ozone. The rate of this process depends on the mechanical strength of the rubber. The continuous alternation of these two stages of the process effects a gradual deepening of the cracks and finally leads to rupture of the rubber. The



TABLE 1

Values of  $\epsilon_{\min}$  for Different Rubbers

	$\epsilon_{\min}$	Modulus of elasticity,* kg/cm <sup>2</sup>
Natural rubber	16	12
Elastic vulcanizate of guttapercha	28	10.4
Butyl rubber	(70)	17
Neurite	65	19.5
SKS-30		
Vulcanized for		
30 min	16	7.2
40 min	20	9.7
60 min	33	10.2

\* The static modulus of elasticity was determined 1 hour after loading, i. e., just before the rubbers were submitted to the action of ozone.



Fig. 3. Photograph of ozone cracks formed at large percentage elongations: a) neurite; b) compound NK. The arrow indicates the direction of stretching.

two-stage character of the process of ozone cracking is excellently confirmed by microphotographs of the formation of "longitudinal" cracks in rubbers based on crystallizable compounds (NK, neurite) at comparatively large elongations (300%) (Fig. 3): the photographs show secondary formations, namely, splitting of the rubber along the fibers, between the initially formed transverse cracks.

The existence of a direct relationship between the mechanical strength of rubber and its resistance to the chemical action of ozone explains the effect of stretching on this process. The appearance of a minimum in the strength of the rubbers when exposed to the action of ozone is a consequence of a two-fold influence of stretching: on the one hand increasing elongation increases the strain in the rubber as a result of which breakdown is accelerated,\* on the other hand the degree of orientation and the strength increase with increasing elongation which results in retardation of breakdown [11]. It is of interest to note that in the case of noncrystallizing rubber polymers orienting processes enter into play in the region of small percentage elongations\*\* the positive effect of which on the strength of most rubbers in ozone begins to outbalance the effect of strain already at nominal elongations of 15-20%\*\*\*. The position of the critical elongation,  $\epsilon_{\min}$ , will be determined by the relative effect of stretching on the degree of orientation of the polymer and its effect on the magnitude of the strain. When the effect of stretching on the degree of orientation of two rubbers is the same the value of  $\epsilon_{\min}$  will be lower for the rubber with the higher modulus of elasticity.\*\*\* In the case of two rubbers with equal moduli  $\epsilon_{\min}$  will be greater in the case of the rubber for which stretching has the more pronounced effect on the degree of orientation (Table 1). Since in the case of butyl rubber vulcanizate the effect of stretching on the degree of orientation is considerably less than in the case of compound NK,\*\*\*\* the value of  $\epsilon_{\min}$  of the former is displaced in the direction of greater elongations.\*\*\*\*\* The increasing extent of intermolecular interaction (lessening effect of elongation on the degree of orientation) in the case of guttapercha and neurite as compared with compound NK, as also with the extension of the vulcanization period in the case of compound SKS-30\*\*\*\*\* effects a displacement of  $\epsilon_{\min}$  in the direction of greater values.

\* Current research has established the necessity for characterizing the strength of rubbers not only by the value of the stress at the moment of rupture ( $\sigma$ ), but also by the time necessary to reach that point ( $t$ ). Normally the relation between these two characteristics will be such that  $t$  will decrease with increasing  $\sigma$  [10].

\*\* Along the edges of cracks elongation is greater than the nominal percentage elongation of the given specimen.

\*\*\* The stipulation here is that the rubbers possess the same resistance to static fatigue.

\*\*\*\* This is seen from the fact that crystallization of butyl rubber begins at considerably greater elongations than it does in the case of compound NK.

\*\*\*\*\* In the case of vulcanizates of butyl rubber the time interval preceding rupture under the action of ozone depends markedly on the degree of elongation when this is small (approximately up to 50-60%), while the dependence is less pronounced at greater elongations. As a result, the value of  $\epsilon_{\min}$  in the case of butyl rubber is not very sharply defined and sometimes cannot be detected at all.

\*\*\*\*\* Vulcanized with an oxidizing-reducing system.

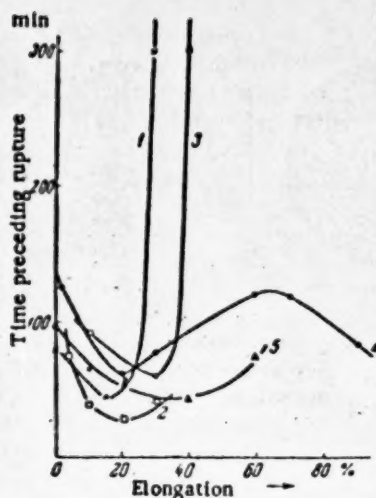


Fig. 4. Effect of elongation on dynamic strength of rubbers: 1) NK, 2) SKS-30, 3) neurite, 4) SKB, 5) butyl rubber.

minimum of the strength is again observed in the case of all the rubbers and the value of  $\epsilon_{\min}$  increases in the order: compound NK - polychloroprene - butyl rubber.

On the basis of the results obtained it is possible to draw the following conclusions.

1. The disruption (cracking) of stretched rubbers, resulting from their chemical interaction with ozone, is a process analogous to the development of static fatigue, in spite of the fact that the rates of these two processes differ by several orders of magnitude. From this it follows that the process of ozone cracking can, in principle, be used as an accelerated method of testing rubbers for static fatigue, particularly at small percentage elongations.

2. The degree of orientation of the structural units of rubbers around the cracks is affected by very small elongations (of the order of 10%). The resistance of rubbers to rupture under the influence of ozone is a sensitive indicator of these changes in orientation. In principle, this phenomenon may be used as a basis of a method of testing the degree of orientation of rubbers.

#### LITERATURE CITED

- [1] R. G. Newton, *Rub. Chem. Techn.* 18, 504 (1945).
- [2] J. Crabtree and A. R. Kemp, *Rub. Chem. Techn.* 19, 712 (1946).
- [3] I. M. Ball, R. A. Jourmans and A. F. Rausell, *Rub. Age* 54, 481 (1944).
- [4] J. Rugg, *Rub. Chem. Techn.* 24, 920 (1952).
- [5] N. N. Znamensky, *J. Tech. Phys.* 30, 1092 (1956).
- [6] E. F. Powell and V. E. Gough, *Trans. IRI* 21, 102 (1945).
- [7] A. Hartman and F. Glander, *Kautsch. u. Gummi* No. 2, 35 (1955).
- [8] Yu. S. Zuev and S. I. Pravednikova, *Trans. Sci. Res. Inst. Rubber Ind.* No. 3, 114 (1956).
- [9] Yu. S. Zuev, *Proc. Acad. Sci. USSR* 93, 485 (1953); 89, 325 (1953).
- [10] S. N. Zhurkov and B. N. Narzulaev, *J. Tech. Phys.* 23, 10, 1677 (1953).
- [11] G. M. Bartenev, *Progr. Chem.* 24, 813 (1955).

Received November 22, 1957

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## THE PHOTOCHEMICAL EFFECT IN THE TRANSFER OF EXCITATION ENERGY IN THREE-COMPONENT SYSTEMS

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(Presented by Academician M. M. Semenov April 25, 1957)

Earlier we have shown that during irradiation with gamma rays of solutions of benzoyl peroxide in benzene there occurs transfer of the primary absorbed energy from the excited benzene molecules to molecules of benzoyl peroxide [1, 2]. As a result, the amount of peroxide decomposed is many times greater than would be expected on the assumption that absorption of energy by each component of the mixture is nonselective. At the same time we have established that addition to the solution of benzoyl peroxide in benzene of small amounts of condensed aromatic hydrocarbons — anthracene and phenanthrene — decreases the rate of the radiolytic decomposition of the peroxide.

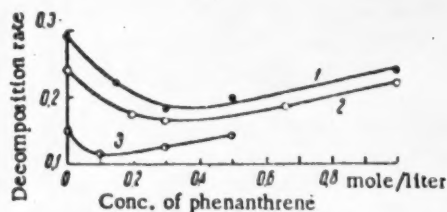


Fig. 1. Dependence of the rate of radiolytic decomposition of benzoyl peroxide, in (mole/liter · hr) · 10<sup>-3</sup>, on the concentration of phenanthrene. Concentration of benzoyl peroxide: 1) 0.0125 mole/liter, 2) 0.0083 mole/liter, 3) 0.0042 mole/liter.

As is known, dilute solutions of anthracene and phenanthrene exhibit fluorescence under the action of ionizing radiations due to energy transfer from the solvent to the solute [3]. The protective action of these luminophors with respect to benzoyl peroxide is, of course, due to the fact that a certain proportion of the excited benzene molecules transmits the absorbed energy to the molecules of the luminophors.

It is a characteristic feature of the process that when the concentration of the luminophors is increased the rate of decomposition of the peroxide attains a certain limiting value and does not decrease any further. This is evidently due to the fact that at sufficiently high concentrations of the luminophors the decrease in the probability of energy transfer in the direction benzene → benzoyl peroxide is compensated by energy transfer according to the scheme: benzene → phenanthrene → benzoyl peroxide.

With the view of carrying out a more detailed investigation of the mechanism of energy transfer during radiolysis of three-component mixtures of benzene, phenanthrene and benzoyl peroxide we have in the present work studied the kinetics of the radiolytic decomposition of benzoyl peroxide in these mixtures over a wide range of concentrations of phenanthrene (0–1 mole/liter) and for three different concentrations of benzoyl peroxide (0.0125, 0.0083, 0.0042 mole/liter).

Radiolysis was effected by means of gamma rays obtained from a Co<sup>60</sup> source in the absence of air. The differential radiation dose was  $1.5 \cdot 10^{15}$  ev/ml · sec. The amount of peroxide decomposed was determined iodimetrically and did not exceed 10–20% of its initial concentration.

In Fig. 1 is shown the dependence of the initial rate of radiolysis of benzoyl peroxide on the concentration of phenanthrene for three different concentrations of the peroxide. As will be seen from the diagram, with increas-

ing concentration of phenanthrene the rate of radiolysis of the peroxide at first decreases and, after having passed through a minimum, increases linearly.

In accordance with the assumptions stated above let us now consider the following elementary processes which take place during radiolysis of the solutions under investigation:

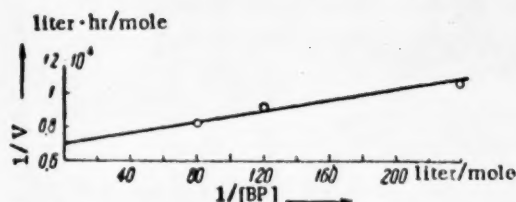
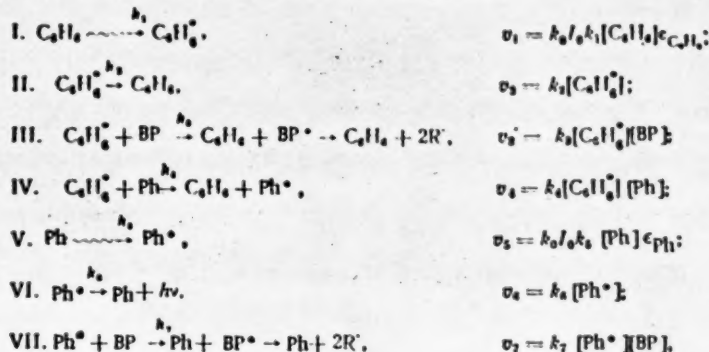


Fig. 2. Dependence of  $1/V$  on  $1/[BP]$ .

formation of radicals from the excited molecules of benzene and phenanthrene is not taken into account because of the low yield of radicals of these hydrocarbons produced by radiation; c) the excited phenanthrene molecules obtained in reactions IV and V are kinetically identical.

In the stationary state we have:

$$k_0 I_0 k_1 [C_6H_6] \epsilon_{C_6H_6} = k_2 [C_6H_6^*] + k_3 [C_6H_6^*] [BP] + k_4 [C_6H_6^*] [Ph]; \quad (1)$$

$$k_0 I_0 k_5 [Ph] \epsilon_{Ph} + k_4 [C_6H_6^*] [Ph] = k_6 [Ph^*] + k_7 [Ph^*] [BP]. \quad (2)$$

Since the rate of the radiolytic decomposition of benzoyl peroxide is given by

$$V = -\frac{d[BP]}{dt} = k_3 [C_6H_6^*] [BP] + k_7 [Ph^*] [BP], \quad (3)$$

the equation of the rate of decomposition of the peroxide may easily be obtained by substituting into (3) the values of  $[C_6H_6^*]$  and  $[Ph^*]$  calculated from (1) and (2).

At sufficiently high concentrations of phenanthrene the processes II and III may be neglected by comparison with process IV. Since under these conditions

$$V \approx k_7 [Ph^*] [BP].$$

where  $I_0$  is the intensity of the incident radiation;  $[C_6H_6]$ ,  $[BP]$  and  $[Ph]$  are the concentrations, respectively, of benzene, benzoyl peroxide and phenanthrene;  $\epsilon_{C_6H_6}$  and  $\epsilon_{Ph}$  are numbers of electrons in the molecules of benzene and phenanthrene, respectively;  $k_0$  is the proportionality constant, and  $R^*$  are the radicals formed in the course of decomposition of the peroxide.

In the scheme of transformations set up above the following simplifying assumptions have been made: a) the concentrations of benzoyl peroxide in the solution being low, the decomposition of the peroxide due to the direct action of the radiation may be neglected; b) the



we have

$$V = \frac{k_0 I_0 k_3 \epsilon_{\text{Ph}} k_7 [\text{BP}]}{k_6 + k_7 [\text{BP}]} [\text{Ph}] + \frac{k_7 k_0 I_0 k_1 [\text{C}_6\text{H}_6] \epsilon_{\text{C}_6\text{H}_6} [\text{BP}]}{k_6 + k_7 [\text{BP}]} \quad (4)$$

For  $[\text{BP}] = \text{const}$ , the second term in Eq. (4) becomes a constant and, consequently, the rate of decomposition of benzoyl peroxide increases linearly with increasing concentration of phenanthrene.

On extrapolating the linear portions of the curves in Fig. 1 to the point of their intersections with the axis of ordinates we can determine the free term  $V$  in Eq. (4) for each of the three concentrations of the peroxide (see Table 1).

TABLE 1

$[\text{BP}] \cdot 10^3$ , mole/liter	12.5	8.3	4.2
$V \cdot 10^3$ , mole/liter · hr	0.125	0.110	0.095

Introducing the notation  $I_{\text{C}_6\text{H}_6} = k_0 I_0 [\text{C}_6\text{H}_6] \epsilon_{\text{C}_6\text{H}_6}$ , we obtain

$$\frac{1}{V} = \frac{1}{I_{\text{C}_6\text{H}_6}} + \frac{k_6}{k_7 I_{\text{C}_6\text{H}_6} [\text{BP}]}$$

i. e.,  $1/V$  is a linear function of  $1/[\text{BP}]$  (see Fig. 2). Hence,  $k_6/k_7 = 2 \cdot 10^{-3}$  mole/liter.

It is of interest to estimate the mean life of the excited molecules of phenanthrene transmitting their energy to benzoyl peroxide. If we assume that energy transfer occurs during collisions of the excited molecules of phenanthrene with molecules of the peroxide and that each such collision is effective, the mean life of phenanthrene molecules in the excited state may be calculated by means of the formula

$$k_6/k_7 = 1/4\pi DR\tau, \quad (5)$$

where  $R$  is the half-sum of the effective radii of the molecules of phenanthrene and benzoyl peroxide ( $\sim 5 \text{ \AA}$ );  $D$  is the coefficient of diffusion in benzene ( $\sim 10^{-5} \text{ cm}^2/\text{sec}$ ); and  $\tau$  is the mean life of the excited phenanthrene molecules. Calculation gives a value of  $\tau \approx 10^{-7} \text{ sec}$ .

We may mention that the value of  $\tau$  for the excited molecules of benzene, which determine the decomposition of benzoyl peroxide, at concentrations lower than 0.01 mole/liter, is also equal to  $\sim 10^{-7} \text{ sec}$ , as has been shown earlier [1, 2].

In a number of recent investigations on the fluorescence of solutions of organic substances [4-6], it has been shown that in many cases there occurs resonance transfer of energy from the excited molecules of the solvent to molecules of the luminophor.

Bowen and Brocklehurst [7] consider that in solutions of organic substances resonance transfer of energy occurs over distances of  $\sim 50 \text{ \AA}$ .

If it is assumed that during resonance transfer of energy relationship (5) remains correct [5], a mean life of  $\tau \approx 10^{-8} \text{ sec}$  is obtained for the excited molecules both of benzene and phenanthrene during resonance transfer of energy, taking  $R = 50 \text{ \AA}$ .

The authors wish to express their gratitude to Prof. S. S. Medvedev for his interest in this work.

#### LITERATURE CITED

- [1] V. A. Krongauz and Kh. S. Bagdasaryan, Proc. Acad. Sci. USSR 114, 4, 829 (1957).\*
- [2] V. A. Krongauz and Kh. S. Bagdasaryan, Collected Papers on Photochemistry, 1957 (in the press).\*
- [3] H. Kallman and M. Furst, Phys. Rev. 79, 857 (1950).
- [4] E. Bouwen and R. Livingston, J. Am. Chem. Soc. 76, 6300 (1954).

\* Original Russian pagination. See C. B. translation.

\*\* In Russian.

[5] T. P. Belikova, M. D. Galanin and Z. A. Chizhikova, *Bull. Acad. Sci. USSR, Phys. Series* 20, 384 (1956).\*

[6] R. Hardwick, *J. Chem. Phys.* 26, 323 (1957).

[7] E. Bowen and B. Brocklehurst, *Trans. Farad. Soc.* 49, 1131 (1953).

Received April 25, 1957

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\* Original Russian pagination. See C. B. translation.

# KINETIC EQUATIONS IN THE THEORY OF ELECTROLYTES

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(Presented by Academician N. N. Bogolyubov, May 7, 1957)

As is well known, the essential point in the derivation of the kinetic equations of Onsager [1] is the assumption that every ion is surrounded by a so-called "ionic atmosphere" composed of ions of opposite sign, which accompanies this ion in its motion. However, it is clear that such a "model concept" cannot be regarded as fully satisfactory from the physical point of view and does not help in obtaining more exact equations.

The present paper examines the general problem of the derivation of kinetic equations for distribution functions of the probability of position of particles situated in a liquid and interacting mutually in a given potential field. The interaction of the particles with the liquid constitutes a kind of stochastic process of a diffusional character.

The given problem can be solved by a statistical method due to N. N. Bogolyubov [2]. The essential feature of this method that instead of dealing with the Gibbs distribution function of all  $N$  particles of the system we are considering a multiplicity of distribution functions for groups of  $s$  particles, the distribution of the remaining  $N-s$  particles being quite arbitrary.

The general outline of the method can be applied to the case of a strong electrolyte. As a first approximation we obtain the well-known equations of Onsager.

Let us consider a system consisting of particles of  $m \geq 2$  different species. Let the number of particles of species  $a$  be denoted by  $N_a$ , so that

$$\sum_{1 \leq a \leq m} N_a = N.$$

The particles are moving in a liquid of volume  $V$  under an external field having the potential  $U_a(t, q_a)$ ,  $q \{ q^\alpha \}$ , and interact mutually in pairs with a potential force of  $\Phi_{ab}(|q_a - q_b|)$ . In deriving our equations we shall assume that as a result of the interaction of the particles with the erratically moving molecules of the liquid the motion of the particles themselves takes place in accordance with the Markovsky stochastic process and can be described by means of the diffusion equation:

$$\frac{\partial D_N}{\partial t} = \sum_{\substack{1 \leq a \leq 3 \\ 1 \leq i \leq N_a \\ 1 \leq a \leq m}} \frac{\theta}{\lambda_a} \frac{\partial}{\partial q_i} \left\{ \frac{\partial D_N}{\partial q_i} + \frac{1}{\theta} \frac{\partial U_N}{\partial q_i} D_N \right\}. \quad (1)$$

In this equation  $D_N = D_N(t, q_1, \dots, q_N)$  denotes the probability distribution function of all the  $N$  particles of the system at time  $t$ ,  $\lambda_a$  is the coefficient of resistance in the expression for Stokes viscous drag,  $\theta = kT$  is the heat function and  $U_N$  is the potential energy of the system, that is

$$U_N = \sum' \Phi_{ab}(|q_i - q_j|) + \sum_{\substack{1 \leq i \leq N_a \\ 1 \leq a \leq m}} U_a(t, q_i). \quad (2)$$

In this expression  $\Sigma'$  denotes summation over all the different pairs of particles.

We shall now introduce the distribution functions  $F_{a_1 \dots a_s}(t, q_1 \dots q_s)$ , determine them in the same manner as has been done by Bogolyubov [2], and derive the corresponding equations of these functions from Eq. (1). On passing to the limits, as usual, that is,  $N \rightarrow \infty$ ,  $V \rightarrow \infty$ ,  $N/V = n$ , these equations will assume the form:

$$\begin{aligned} \frac{\partial F_{a_1 \dots a_s}(t, q_1 \dots q_s)}{\partial t} = & \sum_{\substack{1 \leq j \leq s \\ 1 \leq l \leq s}} \frac{\theta}{\lambda_{a_j}} \frac{\partial}{\partial q_j^2} \left\{ \frac{\partial F_{a_1 \dots a_s}}{\partial q_j^2} + \frac{1}{\theta} \frac{\partial U_{a_1 \dots a_s}}{\partial q_j^2} F_{a_1 \dots a_s} \right\} + \\ & + \sum_{\substack{1 \leq j \leq s \\ 1 \leq l \leq s \\ 1 \leq l' \leq s}} \frac{n_{a_{l'}}}{\lambda_{a_j}} \frac{\partial}{\partial q_j^2} \int \frac{\partial \Phi_{a_j a_{l'}}(|q_j - q'|)}{\partial q_j^2} \cdot F_{a_1 \dots a_s, a_{l'}}(t, q_1 \dots q_s, q') dq', \\ & s = 1, 2, \dots \end{aligned} \quad (3)$$

where  $U_{a_1 \dots a_s}$  is the potential energy of the system of  $s$  separate particles.

To these differential equations we must now add the conditions of disintegration of assemblages of particles. These conditions mean that when a given assembly of  $N$  particles is broken up into two groups of  $s$  and  $\sigma$  particles each, respectively, then the distribution function for the total assembly of particles will have the form of the product of the distribution functions of each separate group when the groups are infinitely removed from each other, that is,

$$F_{s+\sigma} = F_s F_\sigma.$$

We shall now assume that the particles under consideration are electrolyte ions moving in an electric field at a potential which depends on time only, that is,  $E(t)$ , so that

$$e_a E^x(t) = - \frac{\partial U_a(t, q)}{\partial q^x}, \quad (4)$$

where  $e_a$  is the charge of an ion of the  $a$ -th species; the total charge of the ions is equal to zero and the ions interact in pairs with forces defined by the Coulomb potential

$$\Phi_{ab}(|q_a - q_b|) = \frac{e_a e_b}{K|q_a - q_b|}, \quad (5)$$

where  $K$  is the dielectric constant of the solution. Since we shall subsequently confine ourselves to the derivation of equations of the first degree of approximation we shall leave out from consideration the potential due to short-range forces.

Let us consider translationally invariant solutions:

$$F_{a_1 \dots a_s}(t, q_1 + x \dots q_s + x) = F_{a_1 \dots a_s}(t, q_1 \dots q_s); \quad F_a(t, q) = 1.$$

In this case Eq. (3) for  $s = 1$  becomes an identity since

$$\int \frac{\partial \Phi_{ab}(|q_1 - q_2|)}{\partial q_1^2} \cdot F_{a,b}(t, q_1, q_2) dq_2$$

is independent of  $q_1$ .

If now Eq. (3) is treated in the same way as has been done in [4], that is, if we introduce the dimensionless coordinates  $z$ ,  $q^\alpha = r_d z^\alpha$ , where  $r_d$  is the Debye radius, it can easily be shown that the expression  $\partial \Phi / \partial q^\alpha$ , which is a component of the derivative of the potential energy in the second term on the right-hand side of the equation, is proportional to the dimensionless volume  $\epsilon = 1/nr_d^3$  which can be regarded as a parameter of small



magnitude if we take into consideration only solutions of sufficiently low concentrations. The remaining terms in Eq. (3) are of the order of unity relative to  $\epsilon$ .

In order to obtain equations of a first degree of approximation we shall neglect those terms in the exact equations which are proportional to the small parameter  $\epsilon$ . We then obtain the following approximate equations:

$$\begin{aligned} \frac{\partial F_{a_1 \dots a_s}(t, q_1 \dots q_s)}{\partial t} = & \sum_{\substack{1 \leq i \leq s \\ 1 \leq j \leq s}} \frac{0}{\lambda_{a_j}} \frac{\partial}{\partial q_j^2} \left\{ \frac{\partial F_{a_1 \dots a_s}}{\partial q_j^2} - \frac{1}{\theta} e_{a_j} E^* F_{a_1 \dots a_s} \right\} + \\ & + \sum_{\substack{1 \leq i \leq s \\ 1 \leq j \leq s \\ 1 \leq b' \leq m}} \frac{n_{b'}}{\lambda_{a_j}} \frac{\partial}{\partial q_j^2} \int \frac{\partial \Phi_{a_j b'}(|q_j - q'|)}{\partial q_j^2} F_{a_1 \dots a_s b'}(t, q_1 \dots q_s, q') dq'. \end{aligned} \quad (6)$$

$s = 1, 2, \dots$

It can be easily shown that all these equations can be satisfied if we put

$$F_{a_1 \dots a_s}(t, q_1 \dots q_s) = 1 + \sum_{1 \leq i \neq j \leq s} g_{a_i a_j}(t, q_i q_j). \quad (7)$$

In this expression  $g_{ab}(t, q_a q_b)$  are binary functions satisfying the conditions of symmetry,

$$g_{ab}(t, q_a q_b) = g_{ba}(t q_b q_a) \quad (8)$$

and of correlation,  $g_{ab}(t, q_a - q_b) \rightarrow 0$  when  $|q_a - q_b| \rightarrow \infty$ . In view of the translational invariance of the function  $g_{ab}(t, q_a q_b)$  its solutions do not depend on the coordinates themselves, but only on their differences.

Substituting Expressions (7) and (5) into Eq. (6), we obtain:

$$\begin{aligned} \frac{\partial g_{a_1 a_2}(t, q_1 q_2)}{\partial t} = & \sum_{1 \leq i \leq 3} \frac{0}{\lambda_{a_i}} \frac{\partial}{\partial q_i^2} \left\{ \frac{\partial g_{a_1 a_2}}{\partial q_i^2} - \frac{1}{\theta} e_{a_i} E^* g_{a_1 a_2} \right\} + \\ & + \sum_{1 \leq i \leq 3} \frac{0}{\lambda_{a_i}} \frac{\partial}{\partial q_i^2} \left\{ \frac{\partial g_{a_1 a_2}}{\partial q_i^2} - \frac{1}{\theta} e_{a_i} E^* g_{a_1 a_2} \right\} + \\ & + \sum_{\substack{1 \leq i \leq 3 \\ 1 \leq b' \leq m}} \frac{n_{b'}}{\lambda_{a_i}} \frac{\partial}{\partial q_i^2} \int \frac{\partial}{\partial q_i^2} \left( \frac{e_{a_i} e_{b'}}{K|q_i - q'|} \right) g_{a_i b'}(t, q_2 q') dq' + \\ & + \sum_{\substack{1 \leq i \leq 3 \\ 1 \leq b' \leq m}} \frac{n_{b'}}{\lambda_{a_i}} \frac{\partial}{\partial q_i^2} \int \frac{\partial}{\partial q_i^2} \left( \frac{e_{a_i} e_{b'}}{K|q_2 - q'|} \right) g_{a_i b'}(t, q_1 q') dq'. \end{aligned} \quad (9)$$

whence:

$$\begin{aligned} \frac{\partial g_{a_1 a_2}}{\partial t} = & \frac{0}{\lambda_{a_1}} \Delta_{q_1} g_{a_1 a_2} + \frac{0}{\lambda_{a_2}} \Delta_{q_2} g_{a_1 a_2} - \frac{e_{a_1} E}{\lambda_{a_1}} \text{grad}_{q_1} g_{a_1 a_2} - \\ & - \frac{e_{a_2} E}{\lambda_{a_2}} \text{grad}_{q_2} g_{a_1 a_2} - \frac{4\pi}{K} \sum_{1 \leq b' \leq m} n_{b'} e_{b'} \left( \frac{e_{a_1}}{\lambda_{a_1}} g_{a_1 b'} + \frac{e_{a_2}}{\lambda_{a_2}} g_{a_2 b'} \right). \end{aligned} \quad (10)$$

This equation is identical with the well-known equation of Onsager. To prove this it is only necessary to replace the functions  $g_{ab}$  by the functions  $f_{ab}$  as has been done by Falkenhagen [3]. The latter functions are related to the former by the simple equation

$$f_{ab} = n_a n_b g_{ab}.$$

The method outlined above may be extended to the derivation of equations of higher degrees of approximation, as has been done by the author [4] for the case of statistical equilibrium.

#### LITERATURE CITED

- [1] L. Onsager, *Phys. Zs.* 28, 277 (1927).
- [2] N. N. Bogolyubov, *Problems of Dynamics in Statistical Physics* (Moscow, 1946).\*
- [3] H. Falkenhagen, *Elektrolyte* (Leipzig, 1953).
- [4] E. A. Streltsova, *J. Exptl.-Theoret. Phys.* 26, 2, 173 (1954).

Received April 27, 1957

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## INDICATION OF RADICALS BY NUCLEAR RESONANCE

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(Presented by Academician V. N. Kondratyev, March 29, 1957)

The height of the signal of nuclear resonance absorption (using the method known as fast scanning) depends on the spin-lattice relaxation time  $T_1$ . A decrease in the value of  $T_1$  produces an increase in the signal.

In 1946 it was shown [1] that relaxation time is strongly decreased if the paramagnetic ions  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , etc. are present in the system. Quantitatively this effect is expressed [2] by the following equation:

$$\frac{1}{T_1} = k \frac{\eta N \mu^2}{T},$$

where  $T_1$  is the relaxation time,  $k$  is a constant whose value depends on the magneto-mechanical properties of the nuclei,  $N$  is the concentration of paramagnetic ions,  $\mu$  is the effective magnetic moment of the ions;  $\eta$  is the viscosity of the liquid;  $T$  is the temperature.

Small additions of paramagnetic ions make it possible to observe resonance absorption signals in samples with large values of  $T_1$ . Free radicals possess an unpaired electron and the corresponding magnetic moment. Naturally it was assumed that the presence of radicals in the system produces an effective decrease in the relaxation time and a corresponding increase in the resonance absorption signal.

A preliminary study of the possibilities of using nuclear resonance to detect free radicals was carried out on autodyne systems being tested in the Chemical Physics Institute of the Academy of Sciences, USSR. A typical oscillogram of the protonic absorption resonance of water containing  $\text{CuSO}_4$ , taken with this apparatus, is given in

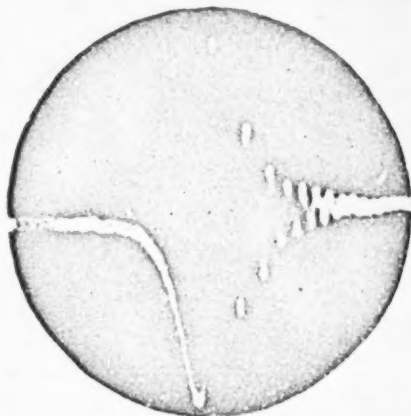


Fig. 1.

Fig. 1. Verification of our assumption on the effect of radicals on the value of the spin-lattice relaxation time naturally began with the simplest case — a solution of a stable radical. Pure benzene did not give a protonic absorption signal on our apparatus. This was due to the fact that the relaxation time of benzene measures several seconds and with the apparatus used it is possible to detect absorption signals from samples having relaxation times of the order of 1 sec and less. We expected that a 0.01 N benzene solution of the free radical diphenylpicrylhydrazyl would give a protonic absorption signal. This expectation, however, was not justified. The decrease in the relaxation time, apparently, was insufficient. We therefore turned to an artificial decrease in the relaxation time by an increase in the viscosity of the system. By this method we obtained the expected result. A solution of diffusion oil in benzene (30% by volume) gave a proton resonance signal at the noise level. The same solution, but containing diphenylpicrylhydrazyl, gave a quite distinct signal.



Fig. 2. Oscillograms of proton resonance signals from decomposing hydrogen peroxide: 1) at  $T = 332^\circ\text{K}$ , 2) at  $T = 368^\circ\text{K}$ .



Fig. 3. Oscillograms of protonic resonance signals from a solution of copper sulfate ( $n_{\text{Cu}^{++}} = 6 \cdot 10^{18} \text{ cm}^{-3}$ ): 1) At  $T = 294^\circ\text{K}$ , 2) at  $T = 368^\circ\text{K}$ .

law  $T_1 \sim \frac{T}{e^{\Delta/T}}$  (the denominator allows for the decrease in viscosity with temperature). An increase in the relaxation time with temperature produces a decrease in the height of the resonance absorption signal. To appraise the scale of the change in the height of the protonic absorption signal with temperature, in Fig. 3 we give reproductions of oscillograms (on the same scale as for  $\text{H}_2\text{O}_2$ ), obtained from a 0.01 M solution of  $\text{CuSO}_4^{**}$  at two temperatures.

The anomalous temperature dependence of the height of the protonic absorption signal in the case of decomposing  $\text{H}_2\text{O}_2$  is quite natural as increasing the temperature leads to a strong increase in the concentration of radicals.

A most important observation, agreeing with the results we obtained, is the fact that there is a strong decrease in the relaxation time in some solid samples treated with high energy radiations [4]. Treatment with radiation leads to the formation of F-centers — holes in the crystal lattice, occupied by free electrons. In its physical nature, an F-center is similar to a free radical. In particular, it gives the effective signal of electronic resonance absorption.

A decrease in the relaxation time is observed: a) on adding the free radical diphenylpicrylhydrazyl to the system; b) in the decomposition of  $\text{H}_2\text{O}_2$ , during which  $\text{OH}$  and  $\text{HO}_2$  radicals are generated; c) in samples containing F-centers — all these confirm our assumption that radicals effectively influence the relaxation time and may be detected by nuclear magnetic resonance.

\* As the decomposition of  $\text{H}_2\text{O}_2$  is accompanied by the evolution of oxygen, which possesses paramagnetic properties, and there is the possibility that the "appearance" of the signal is explained by solution of oxygen in the water, we carried out special calibration experiments. We prepared ampules containing water and oxygen dissolved under various pressures ranging from 4 to 50 atmos. Comparing the height of the protonic resonance absorption signals, obtained from  $\text{H}_2\text{O}_2$  and from solutions of  $\text{O}_2$  in water at the same temperatures, we found that the height of the signal from  $\text{H}_2\text{O}_2$  at  $95^\circ$  corresponded to the amount of oxygen dissolved in water under a pressure greater than 50 atmos. The question of the possibility of supersaturation of water with oxygen was specifically investigated by Seylor [3]. The results of his work show that 50-fold supersaturations, even without mixing, are impossible.

\*\* The paramagnetic ion  $\text{Cu}^{2+}$  was chosen for comparison as its effective magnetic moment is closest to the value of the magnetic moment of radicals.

It seemed to us that it would be possible to observe the effect on a greater scale in the case of simpler radicals. Since simple radicals are not stable we naturally turned to a chemical reaction as a source of such simple radicals. In choosing a reaction in which radicals participate, we adhered to two criteria: a sufficiently high reaction rate at not too high temperatures and a large concentration of hydrogen nuclei in the system. With this object, we chose the thermal decomposition of  $\text{H}_2\text{O}_2$  as the reaction. Neither water nor a 30% solution of  $\text{H}_2\text{O}_2$  gave a protonic absorption signal at room temperature. On increasing the temperature we observed the appearance of a protonic absorption signal from decomposing  $\text{H}_2\text{O}_2$ . On further increasing the temperature and, correspondingly, the rate of  $\text{H}_2\text{O}_2$  decomposition, we observed a further increase in the protonic absorption signal. In Fig. 2 we give reproductions of the oscillograms obtained from the decomposition of  $\text{H}_2\text{O}_2$  at two temperature values.\*

The formula given above shows that on increasing the temperature the relaxation time will increase by the



This method of indication of free radicals, which is less sensitive and accurate than the direct method of electronic paramagnetic resonance, can apparently supplement the latter and broaden its possible use (in particular, for example, in the study of radicals in media with high electrical conductivity).

In conclusion we would like to thank V. V. Voevodsky for continuous interest in the work and valuable discussions.

#### LITERATURE CITED

- [1] F. Bloch, W. W. Hansen and M. Packard, *Phys. Rev.* **70**, 474 (1946).
- [2] N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).
- [3] C. A. Seylor, *Chem. News* **67**, 87 (1893).
- [4] W. Heitler and E. Teller, *Proc. Roy. Soc.* **155 A**, 629 (1936).

Received March 18, 1957

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## APPLICATION OF THE THERMAL FACTOR IN GAS CHROMATOGRAPHY

A. A. Zhukhovitsky and N. M. Turkeltaub

(Presented by Academician P. A. Rebindar, May 10, 1957)

Although there has been a considerable number of investigations in which the thermal factor has played a part in adsorption separation [1-3, 8, 9], there has been no physicochemical analysis of the problem.

The use of the thermal factor in chromatography introduces a series of advantages. Changes in the temperature of the adsorbent bed allow variations in its capacity and make it possible to separate a greater number of components on one adsorbent and achieve a continuous separation process [4, 5]. However, the increase in the distance between the bands of the adsorbate and their contraction is of greater value. Furthermore, in adsorption analysis, the thermal factor can sharply decrease the requirements of sensitivity and inertia of the detecting apparatus.

The advantages of chromatography are used most fully in introducing the thermal factor into development chromatography. The intereffect of the solvent current and any temperature field that changes with time and space, is called chromathernography [6].

It is useful to examine first the relation of the separating capacity to temperature in development analysis.

Separation in development analysis depends little on the temperature of the bed. A simple calculation leads to the following relations for the distance between components ( $\Delta x$ ) and the band width ( $W$ ) on the bed  $\Delta x = \frac{L\Delta Q}{RT}$ ,  $W = \left(\frac{mDL}{\alpha}\right)^{1/2}$ . Here  $\Delta Q$  is the difference in the heats of adsorption of the components,  $D$  is the coefficient of longitudinal diffusion,  $L$  is the length of the bed,  $\alpha$  is the linear flow rate,  $m = 4 \ln(c_{\max}/c)$ , where  $c_{\max}$  and  $c$  are concentrations at the maximum and at the edge of the band, respectively. All distances are changed by a factor  $G$  on the emergent curve ( $G$  is the adsorption coefficient) as compared to the adsorbent bed. Therefore, the detector acts somewhat as an amplifier, changing both  $\Delta x$  and  $W$ . To characterize the separation on a bed from the data from the emergent curve, it is useful to consider the coefficient  $K$  which does not depend on the outlet temperature:  $K = \frac{\Delta x}{(W_1 + W_2)}$ .

It is not difficult to show that the purity of the fraction for the linear isotherm is simply expressed in terms of the coefficient  $K$ :  $\delta = \frac{e^{-4K^2}}{4K\sqrt{\pi}}$ , where  $\delta$  is the portion of foreign component in the fraction.

Glueckauf [7] and other authors [8] suggested analogous operating criteria for the bed based on the concept of theoretical plates. We considered it more advantageous to use investigations of the physical processes of separation and spreading of the bands of adsorbate.

In partition chromatography the diffusion coefficient  $D$  decreases with falling temperature and as with a curvilinear isotherm, the width of the band increases sharply with falling temperature.

A temperature field, independent of time, does not result in better separation. In this  $\Delta x = \frac{\bar{\Delta Q}}{R} \left(\frac{1}{T}\right)$  and the process proceeds as at some average temperature. An analogous result is obtained with a field depending only on time [9,10].

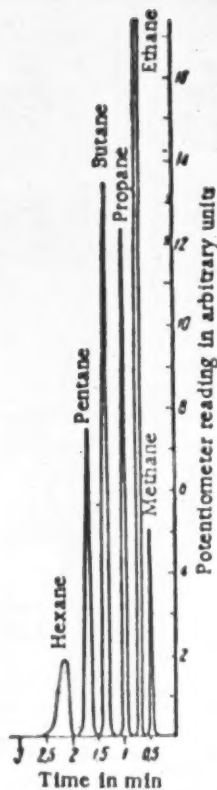


Fig. 1.

Figure 1 gives the emergent separation curve of the mixture  $\text{CH}_4\text{--C}_2\text{H}_6\text{--C}_3\text{H}_8\text{--C}_4\text{H}_{10}\text{--C}_5\text{H}_{12}\text{--C}_6\text{H}_{14}$  in 3 minutes with a temperature change from 20 to 100°.

An increase in the separating capacity from applying the thermal factor may be achieved only with the condition that the components are at different temperatures during the whole experiment and that the average development temperature would thus be different for each component. This can be accomplished by two most advantageous variants of chromathermography. In stationary chromathermography, besides the solvent current, a temperature wave, moving in the direction of the current, would affect the adsorbate. The sign of the temperature gradient would also coincide with the sign of the speed of the developer current. Thus, all components in a stationary system would be at their characteristic temperatures. The basic advantages of this variant consist of the contraction of bands near the characteristic position in the temperature field up to a certain stationary width. This makes the method especially useful for the analysis of materials at low concentrations. Its application substantially lowers the requirement of detector sensitivity.

As was shown in [5], on this basis a continuous analysis could be accomplished. As in development chromatography, in principle any binary mixture can be separated with stationary chromathermography as the distance between the bands is inversely proportional to the temperature gradient, while the band width [12] is inversely proportional to the square root of this value. Therefore, in principle, it is possible by decreasing the gradient (i. e., increasing the length of the furnace) to attain a separation of bands of materials which are as close as one wishes in adsorbency.

However, with a given bed length in stationary chromathermography, the distance between bands will be less than in the development method as the component that is more strongly adsorbed is at temperatures which

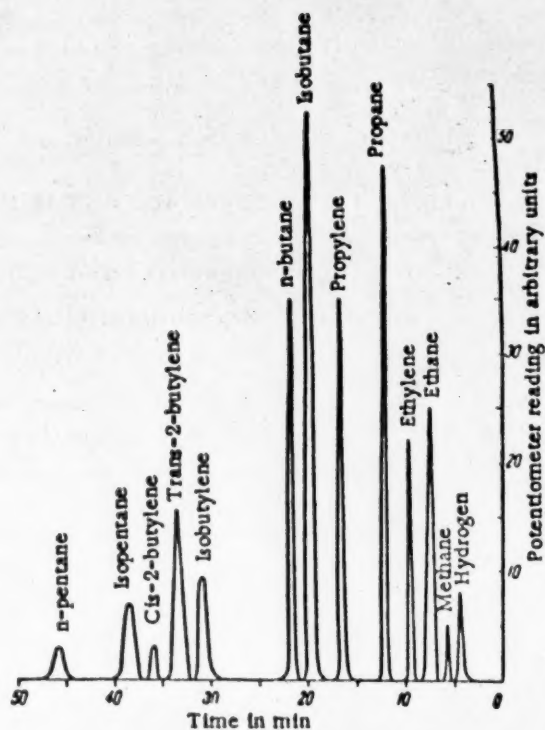


Fig. 2.

However, the simplicity of creating such a field and the possibility of separating a large number of components in a short time give this variant a series of practical advantages.

are higher than those for the one that is less strongly adsorbed. This does not mean, generally speaking, that the separating capacity [13] of stationary chromatography is less than that of the development method, as in the first case contraction of the bands occurs while in the second — spreading of the bands.

It is useful to examine the variants of chromatography in which an increase in the distance between bands, as compared to those of the development method, occurs. To achieve this, it is necessary to localize the component which is less strongly adsorbed in the region of temperatures higher than those for the more strongly adsorbed component. This means that the temperature gradient should have a sign opposite to the flow rate. With this the process is no longer stationary. A "reverse" gradient may be achieved by two methods. In the first of them, the direction of the temperature wave coincides with the direction of the current. Then the more strongly adsorbed components are cooled progressively, and their movement is retarded. This variant has been named adsorption retardation [14]. Only the movement of those components whose starting temperature was lower than the characteristic would be accelerated.

TABLE 1

Adsorbent  $\text{Al}_2\text{O}_3$  16.55 g. Length of tube 250 cm; cross section  $0.125 \text{ cm}^2$ ;  
 $w = 20.8 \text{ cm/min}$ ;  $\alpha = 320 \text{ cm/min}$ ;  $\eta = 0.065$

Expt. no.	Mixture component	Character of temp. gradient	Experimental temp., °C	Peak height, cm	Retaining capacity per $\text{cm}^2$ of cross section	Band width, $w$ , cm	Distance between maxima $\Delta x$ , cm	$K$
20	Propane	forward	120	33	2640	91	240	1.39
21	Butane	reverse	120	46.8	2910	82	240	1.39
21	Propane	reverse	120	9.2	2016	272	1920	4.1
23	Butane	forward	78	23	4250	205	368	1.7
22	Propane	reverse	78	45.6	2640	82	368	1.7
22	Butane	reverse	78	21.6	3008	120	2240	4.5
24	Propane	forward	40	16.8	2350	228.5	640	2.8
24	Butane	forward	40	20.9	4500	183	640	2.8
25	Propane	reverse	40	67.2	2570	64	3250	5
25	Butane	reverse	40	46.4	3312	137	3250	5
				16.8	2590	320		
				5.1	5840	330		

The disadvantage of this variant is the difficulty in ensuring suitable conditions in succession for the different components. The method of selecting the optimal starting temperature [14] has a series of practical defects. Furthermore, one should consider the danger of the disintegration of a component's band into several bands.

In the second variant the direction of the temperature wave is contrary to the direction of the solvent current. Thus, all the components move faster and are washed out in one cycle of the operation.

It can be shown that with a small reverse gradient, the acceleration is related in the following way to the rate of the current  $\alpha$  and Henry's coefficient  $q = \frac{\alpha^2 \sigma}{G}$ . Here  $\sigma = \frac{Q\gamma}{RT}$ , where  $Q$  is the heat of adsorption and  $\gamma$  is the temperature gradient.

In this way, the additional acceleration, which also decreases with increase in adsorbency, would improve separation. This situation is illustrated by the data in Table 1, from which it can be seen that the distance between bands is increased by changing the gradient sign. This increase cannot be wholly due to the effect of the outlet temperature as can be seen from the sharp growth of  $K$ .

We should note that the application of nonstationary chromatography makes the adsorbent column in certain respects more effective than the partition, as with it not only are the isomers of butane and pentane separated but also saturated and unsaturated hydrocarbons and gases with low boiling points. Figure 2 shows the emergent curve of such a mixture.



A disadvantage of the method examined using a reverse gradient is that all components pass through the same temperature regions. The retardation variant may be used only under automatic conditions which could be achieved by the reverse movement of the furnace to the starting temperature, with a repetition of the cycle. Thus, due to the movement of the components into the depth of the furnace, they would gradually reach the critical state and their movement would be accelerated.

The thermal effect could be used not only as a continuously operating field but also as short duration heating (impulses) with subsequent cooling. In the development method an increase in the length of the adsorbent bed cannot be practically achieved due to the spreading of the bands and the limited sensitivity of the detector. If, however, after development on a certain length of the adsorbent bed, the adsorbate is treated with a "collecting" heat impulse then the length of the adsorbent bed may be increased without limit.

It is advantageous, in impulsive chromatography of a mixture, to bring about circulation, returning the component after the impulse to the beginning of the bed. At the end of the bed there should be a thin "collecting" bed of an adsorbent with a high adsorbing capacity, onto which the impulse would be directed at the necessary moment. The feeding of the impulse should be regulated in relation to the degree of separation required. At the minimum on the emergent curve an impulse should be fed in, and the enriched mixture should be introduced onto the adsorbent for subsequent circulation. Such a form of temperature field, depending on the degree of separation, we have named "self-adjusting." On the basis of such fields, it is possible to obtain the best separations and to establish a programme for the separating adsorbent-thermal machine.

The automatic equipment should control such factors as the distribution of temperature, variation of rate, etc. Based on the automatically calculated value of  $K$  or of a similar magnitude, after a certain period during which ordinary development analysis would be carried out, a temperature field with reverse gradient would be automatically introduced onto the bed of adsorbent material and its magnitude would be changed automatically in relation to time; moreover,  $K$  would increase continuously.

#### LITERATURE CITED

- [1] P. Shuftan, *Gas Analysis in Technology* (Kharkov, 1933).\*
- [2] G. G. Grigoryev, M. I. Subbota, N. M. Turkeltaub and B. P. Yacenev, *Gas. Core Gas Prospecting and Gas Analysis* (1954).\*
- [3] A. Eucken and H. Knick, *Brennstoff Chem.* 17, 241 (1946).
- [4] C. Berg, *Trans. Am. Inst. Chem. Eng.* 42, 665 (1946).
- [5] A. A. Zhukhovitsky, N. M. Turkeltaub and T. V. Georgievskaya, *Proc. Acad. Sci. USSR*, 92, 937 (1953).
- [6] A. A. Zhukhovitsky and N. M. Turkeltaub, *Proc. Acad. Sci. USSR* 94, 77 (1951).
- [7] E. Glueckauf, *Trans. Farad. Soc.* 51, 34 (1955).
- [8] C. G. S. Phillips, *Gas Chromatography* (London, 1956).
- [9] M. R. Hoare and J. H. Purnell, *Trans. Farad. Soc.* 52, 222 (1956).
- [10] A. K. Wiebe, *J. Phys. Chem.* 60, 685 (1956).
- [11] N. M. Turkeltaub and V. P. Shvartsman, *J. Phys. Chem.* 27, 1827 (1953).
- [12] A. A. Zhukhovitsky and N. M. Turkeltaub, *Progr. Chem.* 35, 7, 859 (1956).
- [13] N. M. Turkeltaub, *Proc. Commission on Anal. Chem., Acad. Sci. USSR Press* 6, 147 (1955).\*
- [14] A. A. Zhukhovitsky, E. V. Vagin and S. S. Petukhov, *Proc. Acad. Sci. USSR* 102, 771 (1955).

Received May 8, 1957

\* In Russian.

## THE NATURE OF THE SURFACE OF DEHYDRATED SILICA GEL

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(Presented by Academician M. M. Dubinin, May 4, 1957)

Starting from the structural principles of the atomic structure of silica and silicates, it was shown in paper [1] that in the thermal dehydration of silica, a surface may be formed which contains oxygen atoms in excess of the stoichiometric ratio. Some experimental data, confirming this idea, were given in paper [2]. It was to be expected that such a surface would possess oxidizing properties. We noted long ago that in adsorbing a series of organic materials that give colored oxidation products silica gel, which had been calcined in air, became colored, and the intensity of coloring increased with an increase in the calcination temperature. It seemed interesting to carry out the quantitative determination of the oxidation capacity of a silica gel surface in relation to its calcination temperature.

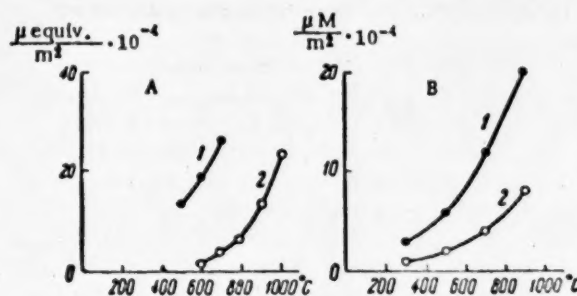
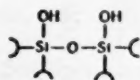


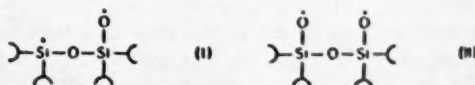
Fig. 1. Oxidation capacity (A) and oxygen sorption (B) of silica gels KSK-2 (1) and K-2 (2) in relation to their calcination temperature.

obtained that the oxidation capacity of the surface is very small, the number of oxidizing equivalents is three orders less than the number of OH-group equivalents on the same surface [3]. It can be seen from Fig. 1A that the oxidation capacity of the surface is different for samples with different degrees of hydration: it is greater for sample KSK-2, which has a smaller value for the specific surface and greater hydration. The number of oxidizing equivalents increases for each of the samples with an increase in calcination temperature.

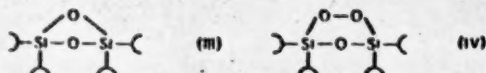
In the thermal dehydration in vacuum of an element of hydrated silica surface:



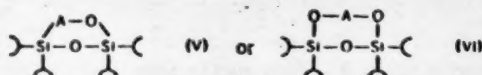
It is possible to form the following surface radicals or free valencies [1]:



which are accompanied by liberation of water (I) or hydrogen (II). It was established by mass-spectroscopic investigations of the dehydration of silica gel (sample K-2), as well as chemical analysis [6-7] of the gas uncondensed by liquid air, that besides water, hydrogen is present in the products liberated by silica dehydration. The fall in adsorption activity when silica gel was dehydrated in vacuum [8] indicated that a large part of the free radicals were, apparently, blocked:



In the dehydration of the surface in an atmosphere of some gas (A), the reaction of the molecules of this gas with the active centers of the surface may result in surfaces of a completely different type than in (I-IV), for example:



In this way, in the case of thermal dehydration of silica gel in air, as was done in works [3-5], the possible adsorption of nitrogen and oxygen resulted in a surface substantially different from the surface obtained in vacuum.

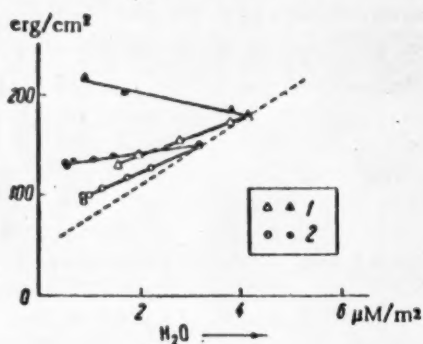


Fig. 2. Heats of wetting of silica gels KSK-2 (1) and K-2 (2), calcined in air (white dots) and in vacuum (black dots) in relation to the hydration of their surfaces. The broken line represents data corresponding to the standard treatment of silica gel surfaces [3].

Indicates that the number of the latter is not great. Apparently, the oxidizing properties of the silica surface are developed due to the hydration of elements (II) and (VI). A comparison of the data on the oxidizing properties of the surface and adsorption of oxygen on it for the same samples and the temperatures at which they were treated, shows that for all cases investigated the number of oxidizing equivalents is twice as great as the number of moles of oxygen adsorbed. The symbatic character of the changes in the oxidizing capacity of the surface and the adsorption of oxygen on it shows that the same centers of the surface are, probably, responsible for both phenomena. If the surface elements (II) are such centers for oxygen adsorption then, apparently, there should be a definite relation between the amount of hydrogen liberated from the surface during its dehydration and the amount of oxygen adsorbed on it. With this, however, one should keep in mind the fact that the amount of hydrogen liberated may exceed the amount of oxygen adsorbed due to the disappearance of a certain amount of the radicals formed, as a result of the contraction of the surface during calcination, as well as due to the blocking of bonds with the formation of surface elements (IV). Preliminary experiments, carried out by calcining in vacuum at up to 800° silica gel samples which were first pumped out at 300°, showed that the amount of hydrogen thus liberated, considering it as the gas that did not freeze out at the temperature of liquid nitrogen [6, 7], exceeded by 2-3 times the amount of oxygen which was later adsorbed on the same surface.

To clarify these problems, we carried out quantitative measurements of the adsorption of nitrogen and oxygen on silica gels dehydrated under conditions of high vacuum. The measurements were carried out by a volumetric method. A sample of silica gel was placed in a quartz ampule and after preliminary conditioning at 300°, was calcined at the given temperature up to constant vacuum, then a prepared portion of the gas being investigated was introduced into the ampule and suitable measurements were carried out at 20°. As our experiments showed, nitrogen under these conditions was not adsorbed within the limits of accuracy of the measurements ( $1 \cdot 10^{-4} \mu\text{M}/\text{m}^2$ ). In the case of oxygen (Fig. 1B), the surface of silica gel, dehydrated in vacuum at temperatures from 300 to 900°, adsorbed oxygen noticeably, and the amount of oxygen sorbed increased with increased calcination temperature. The small value of adsorption of oxygen, which, presumably, is adsorbed at the surface radicals,

Previous experiments [9] showed that irradiation of the silica with ultraviolet light produced the formation on its surface of free valencies (scheme II) which were centers of oxygen adsorption. Our measurements of photo-desorption and subsequent adsorption of oxygen after irradiation of silica gel K-2 with the light of a mercury lamp PRK-4 fully confirmed these results. The effect of short wave irradiation and thermal dehydration, apparently, result in a surface which, on the whole, is the same in its properties. On the contrary [10], free radicals may be formed not only as a result of irradiation but also by calcining silica in vacuum.

In connection with the presence of adsorption centers with high activity on the surface of silica dehydrated in vacuum, the energetic properties of such samples should differ from the corresponding properties of samples calcined in air. For this purpose, we investigated the heats of wetting with water of silica gels, calcined in vacuum at various temperatures up to 800°. The silica gel was calcined in a quartz ampule, connected to a glass pig with small ampules sealed to it for determining structural water, specific surface and heats of wetting. The pig was unsealed from the vacuum apparatus and the silica gel in vacuum was dispersed into the ampules which were then removed. From the data obtained, given in Fig. 2, it can be seen that both silica gels gave a higher heat of wetting after calcination in vacuum than those samples which were calcined in air [3]. The difference between the heats of wetting of samples calcined in air and in vacuum was considerably greater for KSK-2 silica gel which possesses a larger number of active centers than silica gel K-2, in conformity with the data on oxidation capacity and oxygen adsorption (see Fig. 1). The heat of wetting of KSK-2 silica gel, contrary to the case when it is calcined in air, increased with dehydration of the surface. It follows from this that on the surface of silica gel dehydrated in vacuum, centers are formed with a higher adsorption activity than OH groups.

The data obtained by us is in agreement with the conclusions of the authors of papers [11, 12], in which the presence of centers of high activity (centers of the second type) were established on the basis of investigations of infrared spectra of water adsorbed on porous glass, calcined in vacuum. It must be noted that the difference in surfaces obtained by dehydration of silica gel in air and in vacuum is not limited only to the centers at which oxygen is adsorbed, but spreads, apparently, to other parts of the dehydrated surface. The investigation of these problems will be the subject of a separate report.

The authors would like to thank A. N. Terenin for his interest in the work and valuable advice, as well as B. V. Ilina for her support.

#### LITERATURE CITED

- [1] W. A. Weyl, *Res.* 3, 230 (1950).
- [2] E. A. Hauser, D. S. Le Beau and P. P. Pevear, *J. Phys. and Coll. Chem.* 55, 68 (1951).
- [3] M. M. Egorov, K. G. Krasilnikov and E. A. Sysoev, *Proc. Acad. Sci. USSR* 108, 103 (1956).
- [4] M. M. Egorov, K. G. Krasilnikov, V. F. Kiselev, N. V. Kapitonova and E. A. Sysoev, *J. Phys. Chem.* 31, 1448 (1957).
- [5] M. M. Egorov, T. S. Egorova, V. F. Kiselev and K. G. Krasilnikov, *Proc. Acad. Sci. USSR* 114, 3 (1957)\*.
- [6] L. Miller, *Koll. Zs.* 142, 117 (1955).
- [7] W. Stöber, *Koll. Zs.* 145, 17 (1956).
- [8] S. P. Zhdanov, *Surface Chemical Compounds and Their Role in Adsorption Phenomena* (Moscow, 1957), p. 129.\*\*
- [9] A. N. Terenin, *Coll. Problems of Kinetics and Catalysis* 8, 17 (1955).
- [10] A. V. Kiselev, *Coll. Problems of Kinetics and Catalysis* 8 (1955).
- [11] V. A. Nikitin, A. N. Sidorov and A. V. Karyakin, *J. Phys. Chem.* 30, 117 (1956).
- [12] A. N. Sidorov, *J. Phys. Chem.* 30, 995 (1956).

Received May 26, 1957

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\* See C. B. translation.

\*\* In Russian.



PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

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